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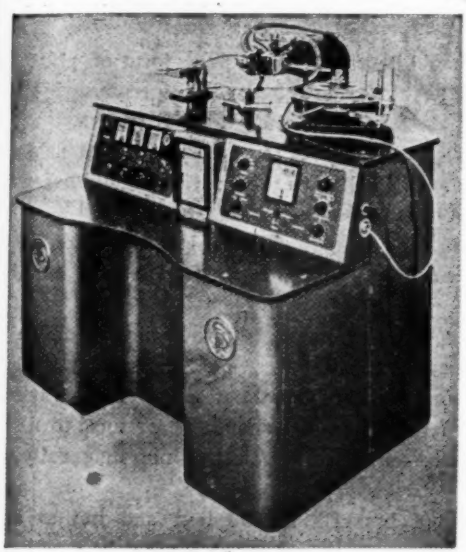

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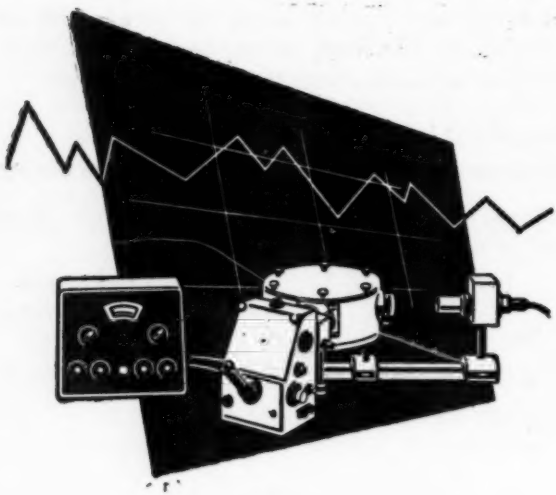

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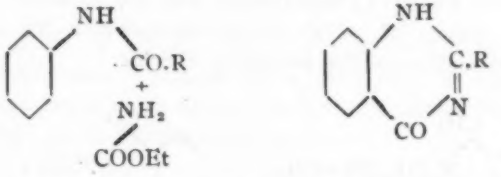
[Jour. Indian Chem. Soc., Vol. 35, No. 10, 1958]

CHEMISTRY OF VASICINE AND CHAKSINE*

By J. N. Ray, D.Sc., Ph.D., F.N.I., F.R.I.C., O.B.E.

Vasicine and Peganine

It was in 1926 that I was asked by Acharya Ray to investigate the active principles of Vasaka. Extract Vasaka was one of the first items to be put in the market by Bengal Chemical & Pharmaceutical Works. In the indigenous system of medicine, Vasaka enjoyed a great reputation as an expectorant and, in fact, claims have been made that it has antitubercular properties. While I was engaged in isolating the alkaloid, Sen and Ghose[1] isolated vasicine, $C_{11}H_{12}ON_2$, a monoacid base. They found it to be converted to chlorodesoxyvasicine with PCl_5, indicating that there was an OH group, replaceable by Cl. With permanganate, a substance, $C_8H_6NO_2$, was isolated. This was suspected to be 4-oxyquinazoline. Later on, Ghose, Krishna, Narang and Ray[2] proved this supposition to be correct by a direct comparison of the oxidation product with synthetic 4-oxyquinazoline. Sen and Ghose[1] had assigned a structure in which vasicine was visualised as 2-propyl (or *iso*propyl)-4-oxyquinazoline, but De and Ray[3] proved that vasicine was not identical with the products synthesised as follows:



Ghose, Krishna, Narang and Ray[2] found evidence that vasicine was converted into an isomeric substance with alkali, but later on withdrew the claim as they were not sure about the purity of the transformation product[4]. They found[2] that vasicine gave a solid dehydro acetyl derivative, m.p. 165°.

In 1934, Späth and Nikawitz[5] were supplied by the firm of E. Merck a base isolated from the mother-liquors of *Peganum harmala* from which they isolated a crystalline product having the same empirical composition as vasicine, which they called peganine. The base melted at about 5° higher than vasicine, but its m.p. was determined in vacuo as it, like vasicine, decomposed on melting. But it was stated that peganine gave a liquid acetyl derivative; hence doubts were expressed by us about the identity of vasicine and peganine. We were not able to secure a specimen of peganine from Vienna. The solubility of vasicine in acetone also differed from peganine. Hanford, Liang and Adams[6] who found the solubility of vasicine in acetone to be small, as found by the Indian workers, also confirmed that the acetyl derivative was not a liquid, but a solid, having the same m.p. as found by us. Späth *et al.* later on agreed that the acetyl derivative was a solid. Finally Späth and Kuffner[7] definitely

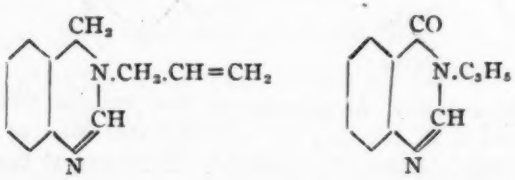
* Eleventh Acharya Prafulla Chandra Ray Memorial Lecture, delivered on 2nd August, 1958 in Calcutta.

established the identity of the two by direct comparison with a sample supplied from India.

Späth and Nikawitz[5] found that on oxidation of vasicine with permanganate at low temperature, it gave 4-oxyquinazoline-*N*-acetic acid. On this basis they formulated vasicine as:

It may be pointed out that the Indian workers, who had earlier isolated 4-oxyquinazoline as the oxidation product, had stated that the isolation of 4-oxyquinazoline did not mean that an oxygen atom pre-existed in this position, as quinazolines were known to acquire an oxygen atom in this position during oxidation. This observation of theirs proved to be correct as subsequently it was found that vasicine did not have an oxygen atom in the second ring.

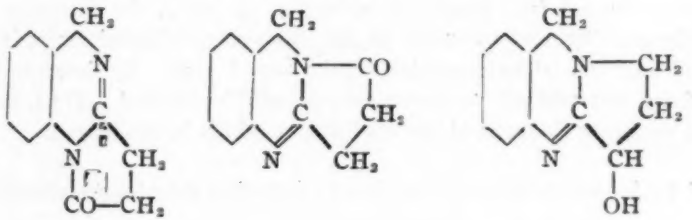
Narang and Ray[6] criticised the Späth formula on various grounds, but mainly because of the fact that 3-allyl-1:3-benzodiazine was not identical with desoxyvasicine, and the reduction product of 3-allyl-4-oxyquinazoline with Na and amyl alcohol was not identical with the similar reaction product of vasicine.



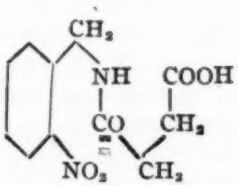
Reynolds and Robinson[9] adduced further proof against the Späth formula and suggested that in view of prior isolation of vasicine, the name peganine should be abandoned. The späth formula depicted vasicine as a carbinol-amine, but it showed no reactions of this class of substances.

The first suggestion, apart from the suggestion of Ghose *et al.*[2] that there was a third ring in *isov*asicine, was that of Hanford *et al*[4]. The presence of an allyl group was never seriously suggested by us. The evidence pointing to this direction was the decolorisation of permanganate by vasicine at 0°, but as against this has to be stated the fact that the reduction of the so-called allyl group is never possible either catalytically or by other means. Vasicine has no rotation, but Ghose *et al.*[2] were able to resolve it, showing that one of the atoms was asymmetric. This result was later confirmed by Späth although they criticised Ray *et al.*[17] for not publishing the full details of the resolution. This we would have done as soon as optically pure samples

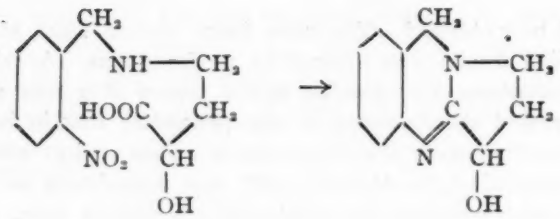
of enantiomorphs had been obtained. The active forms showed signs of auto-racemisation and, hence, full details were withheld by us for a time. At this stage it was agreed by all the contestants that vasicine had a system of 3 ring systems fused together. We had proved the existence of the quinazoline ring by isolating 4-oxyquinazoline first. Thus the novelty of a quinazoline in a plant product was established. The isolation of 4-oxyquinazoline-*N*-acetic acid was undoubtedly an advance, but this had led Späth to rashly postulate the position of the oxygen atom to be OH in the β-position in the third ring. Späth postulated all the possible formulae with 3 rings—one of them was sure to be correct in the long run. In the mean time, Indian workers proceeded on to establish whether the third ring was fused linearly or angularly. Narang and Ray[10] prepared the following and found that the reduction of the linerarly fused ring was identical with the electrolytically reduced product of vasicine.



Therefore the nature of all the rings of vasicine had been understood and established. The Indian workers[15] pleaded for a little time to complete the investigation which they had begun much earlier than the Austrian workers. The Americans withdrew from the field but the Austrians won the race.

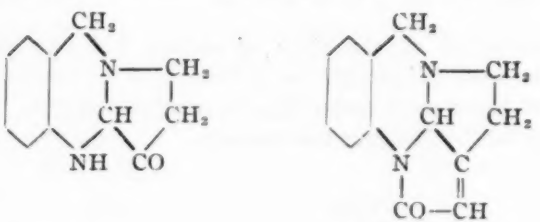


The synthesis of desoxyvasicine by Späth *et al.* is at best at par with the work of the Indian workers and only proves the linear configuration of the third ring. It does not indicate the position of the OH group. Morris, Hanford and Adams[13] furnished an acceptable proof of the position of the OH group. They proved that it was in the α-position and not in β-position, as supposed by the Austrian workers. Now the way was paved for the final synthesis of vasicine. This was a comparatively simple matter as all the details about vasicine were now known to all. The race again was won by the Austrians who condensed *o*-nitrobenzyl chloride with α-hydroxyaminobutyric acid. The product on cyclisation and reduction furnished vasicine.



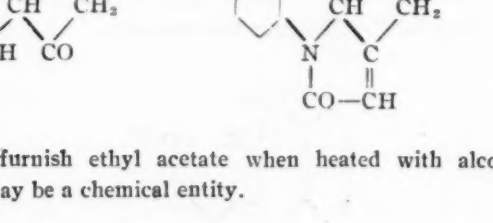
An exactly similar work was in progress at Lahore where the hold-up was due to non-availability of some chemicals. Späth and co-workers stated that no credit was due to the Indian workers for showing the linear character of the third ring as in their hands vasicine, on electrolytic reduction, broke down to *o*-aminobenzylpyrrolidine. Therefore the work of Juneja, Narang and Ray[13] did not prove anything. Narang and Ray[14] gave an adequate reply to this and they showed that the reduction of vasicine took place through four steps: (1) reduction of N=C, (2) formation of an unsaturated substance by loss of water in the third ring, (3) reduction of (2) to the related saturated body and (4) hydrogenolysis of the second ring. By interrupting the current at definite intervals all the four products could be isolated. Thus, the credit for establishing the linear character of the third ring could not be challenged.

In view of the known structure of vasicine, we formulate dehydro-acetylvasicine as:



This substance does not furnish ethyl acetate when heated with alcohol and H_2SO_4. Therefore, *iso*vasicine may be a chemical entity.

The two products isolated from the H_2O_2 oxidation are therefore:



(A) (B)

The conversion of A to B by further oxidation can be understood.

Chaksine

It was in 1935, Siddiqui and Ahmed[16] isolated a quaternary base from the seeds of *Cassia absus* and assigned the formula $C_{12}H_{20}O_2N_3.OH$. But Ray *et al.*[11] suggested that the base should be formulated as $C_{11}H_{20}O_2N_3.OH$ and adduced evidence in support of this view. After a long controversy it is now agreed by all that the formula of Lahore workers is correct[18]. Guha and Ray[19] assigned a tentative structure for chaksine after studying a large number of its degradation products. They relied mostly on I.R. of several of chaksine derivatives. The salient absorptions were in the regions noted below:

6.35 mμ presence of C=N (formerly questioned by Singh *et al.*,[21] but now admitted to be correct).

3.0 mμ ,, ,, NH (This NH was supposed to be a part of a ureido group absorption at 5.8 and 5.95mμ).

7.22 mμ ,, ,, C—Me.

5.80 mμ ,, ,, CO conjugated ester.

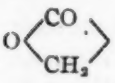
5.95, 6.10 mμ ,, , CO-NH.

7.62, 7.86 mμ ,, ,, $C(=O)-NH-C$.

No proof was given for the bicyclic ring system except that the acids obtained by hydrolysis with baryta on distillation afforded pyrrole. It was recognised that this was a vulnerable point of the formula suggested.

Kamal and Hahn[18] found that when chaksine was heated with alkali, 2 mols. of ammonia were evolved progressively: the first mol. in 40 hours and the second in 240 hours. Therefore it will be seen that the third N atom is differently constituted from the two others. In assigning a structure to chaksine, this fact has to be borne in mind. Kamal and Hahn[18] have also confirmed the transformation of chaksine nitrate to nitrochaksine, observed and described by Ray *et al*[19]. The latter authors were aware of the possibility of this transformation also being of the type guanidine nitrate to nitroguanidine and had indicated this possibility years ago[19]. They gave up this idea in view of some of the model guanidine compounds synthesised at Lahore not behaving at all like chaksine. The I.R. absorption at 5.95, 6.10, 7.62, 7.85 mμ, all pointed out an urea residue being present in chaksine.

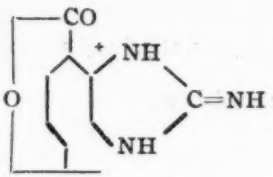
Guha and Ray[19] from the I. R. evidence concluded that probably a COOH was present in the nitrochaksine molecule. This was hotly contested by Singh *et al.*[20]; but Kamal and Hahn[18] found nitrochaksine to be amphoteric, which definitely did not rule out the possibility of a COOH being set free from a lactone ring rendered unstable. We have now found definite evidence that there is a lactone (lactide) ring in chaksine. If chaksine is heated with ammonium acetate (sulphate or chloride can be taken), and then the mixture is diluted with water, a clear solution results. From this on acidification a substance, different from chaksine sulphate, is precipitated. Preliminary

results show it to have $CO.NH_2$ group and CH_2OH formed by the opening of a  group.

Singh *et al.*[21] by treatment with alkali isolated, from chaksine, methylpimelic acid and chaksine acid. The latter has now been formulated as 1 : 2 : 6-heptane tricarboxylic acid[21].

Siddiqui *et al.*[18] have found that by distillation of chaksine with electrolytic Cu, phthalic acid is formed. The aromatic ring has been formed no doubt by pyrolysis, but this proves that 8 C atoms are in a chain.

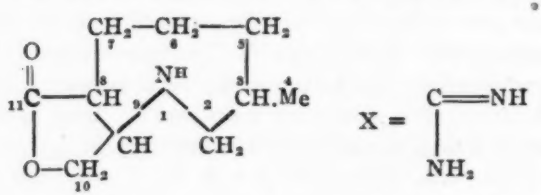
Very recently a group of American authors[22] have formulated chaksine as (I).



(I)

We feel that such a structure is improbable on many grounds as it does not satisfactorily account for the formation of *iso*propylbenzoic acid, α-pimelic acid, phthalic acid etc. The reliance on I.R. for a cyclic urea structure may not be reliable.

We think that in view of (*a*) the difference between the third N and the other two, (*b*) liberatation of CO_2 from chaksine on heating with HCl, (*c*) formation of phthalic acid on pyrolysis, (*d*) formation of methylpimelic acid (this needs confirmation) and (*e*) 1 : 2 : 6-heptane tricarboxylic acid, chaksine can be represented as :



X may be attached to (1) or to (10). The atoms No. 1, 2 and 6 are involved in an intra-annular tautomerism. There may be H bonding between atom No. 6 and No. 1. Chaksine gives HCHO with Fenton's reagent, suggesting the linkage of X at 10.

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[Jour. Indian Chem. Soc., Vol. 35, No. 10, 1958]

EVALUATION OF THE TRUE ZETA-POTENTIAL OF HIDE AND LEATHER DIAPHRAGMS

By B. N. Ghosh and S. Ghosh

The electro-osmotic flow of water through membranes of hide and leather in equilibrium with dilute solutions of NaCl of constant p_H, but of varying specific conductivity, has been studied. The apparant electrokinetic potential ζ_a, calculated from the experimental data, using the Smoluchowski equation, has been found to vary with the specific conductance, K, in bulk of the electrolyte solutions used, according to the equation:

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m.\frac{1}{K} .$$

where m is a constant and ζ represents the true electrokinetic potential. The significance of the results obtained has been discussed.

The electrokinetic or ζ-potential, evaluated from electro-osmotic experiments, may not always represent the true value due to factors like surface conductivity (Bikerman, *Disc. Faraday Soc.*, 1940, 154 ; Rutgers, *ibid.*, p. 69).

Experiments have therefore been undertaken to ascertain if the true ζ-potential of hide and leather diaphragms in solutions, having constant p_H but varying conductivity, effected by changing the concentration of added sodium chloride, a neutral electrolyte having no specific affinity for protein groups, can be determined by the electro-osmotic method. The results obtained are recorded in this paper.

Experimental

Samples selected at random from pieces of limed goat skin and of formaldehyde-, vegetable, and chrome-tanned leathers were used as diaphragms. These were washed free of electrolytes, using conductivity water. The chrome-tanned leather was, however, neutralised in dilute borax prior to washing ; this was necessary, as otherwise it was difficult to obtain an equilibrium solution of constant p_H with the chrome-tanned leather in very dilute borate buffers.

Electro-osmotic Experiments

A simple cell was devised for measuring the rate of electro osmotic flow through hide or leather membranes. The cell consisted of two bored rubber blocks in between which the membrane was held watertight by means of two wooden frames, joined by four screws. The two limbs of the electro-osmotic cell, forming a U-tube together, passed through the bores in the rubber blocks till they came in contact with the leather from the two sides.

The two limbs were filled with the solution, against which the ζ-potential was to be determined and in which the membrane had previously been soaked to equilibrium. The liquid in the limbs was continuous through a narrow flow tube,

so that there was no difference in hydrostatic pressure between the two limbs and also the liquid passing through the membrane during electro-osmosis did not generate any appreciable difference in hydrostatic pressure. The electro-osmotic flow was measured by noting the movement of a small air-buble (0.5 cm) which was introduced into the flow tube while setting up the apparatus with the help of two three-way stop-cocks ; the rate of flow was calculated from the values of the internal cross-section of the tube and the distance moved by the air-bubble in unit time. The flow tube itself was filled with conductivity water and kept horizontal. In this arrangement, the diameter of the tube employed in the cell was small and the bulging of the membrane did not occur.

The flow tube, stop-cocks, as well as the glass parts of the cell were kept in chromic acid prior to experimentation in order to remove grease. This was necessary for ensuring smooth movement of the air-bubble in the flow tube.

The electrical circuit for the electro-osmotic experiment was quite simple. The supply from 220 volt DC mains was dropped to a constant voltage of 105 by using a VR 105 electronic valve. The voltage was applied to the two electrodes dipped into the limbs of the cell through one constant and another adjustable resistances, a milliammeter and a commutator. The resistance was so adjusted as to give a current strength of not more than 10 millamps as otherwise, at the concentrations of the electrolytes in some of the experiments, there was much electrolysis and evolution of gas bubbles which interfered with the measurement.

The experiments were conducted at the room temperature, which was always noted, since this was necessary for securing the viscosity of the liquid at this temperature.

Pieces of goat skin or leather were soaked in 250 c.c. of dilute buffer or dilute acid for 5-7 days for the attainment of equilibrium (*i.e.*, till p_H became constant). Soaked pieces were then fitted up in the cell to act as diaphragms and the electro-osmotic velocity measured. ζ_a was calculated using the value of bulk specific conductivity, K.

After the first experiment, a few drops of dilute sodium chloride solution were added to the soaking solution for obtaining a higher specific conductivity without changing the p_H ; the solution was quickly allowed to flow several times through the membrane fitted in the cell, mechanically or under the influence of an electrical field. The limbs were filled up with the solution containing NaCl and the ζ_a obtained again at a higher bulk specific conductivity of the equilibrium solution.

The p_H of the solution was measured by a glass electrode after each determination of flow, and the p_H did not change more than 0.1 unit throughout the whole range of conductivities studied. The apparant ζ_a potential was calculated by using the Smoluchowski equation :

$$\zeta_a = \frac{4\pi\eta KV}{iD} \times (100)^2$$

where η = coeff. of viscosity, K = sp. conductivity, and D = the dielectric constant of the solution in contact with the diaphragm ; V = volume of liquid passing through dia-

phragm per sec. and i = the current strength. The true ζ-potential was then evaluated from the apparent ζ_a by using the following equation in which the surface conductivity correction was introduced :

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m\frac{1}{K} \qquad \ldots \qquad \ldots \quad (1)$$

where m is a constant which includes sp. surface conductivity (Ghosh, *Trans. Faraday Soc.*, 1953, **49**, 1475 ; this *Journal*, 1955, **32**, 69).

The results of the determination of ζ-potential at a particular p_H and different specific conductivities are recorded in Table I (A−F). ζ represents the corrected value of ζ_a.

TABLE I

Electro-osmosis through variously tanned leather.

K(mho cm^{-1}).	ζ_a. (mv)	$1/K$.	$1/\zeta_a \times 10$.	ζ(from graph).	K(mho cm^{-1}).	ζ_a. (mv)	$1/K$.	$1/\zeta_a \times 10$	ζ(from graph).
A. Goatskin at p_H 7.35 in borate buffer.					B. Chrome-tanned leather in borate buffer at p_H 6.6.				
8.22×10^{-5}	2.73	12170	3.67		4.29×10^{-5}	18.7	23310	5.35	
3.66×10^{-4}	6.33	2730	1.58	9.52 mv	5.90×10^{-5}	2.38	16940	4.23	7.81 mv
7.63×10^{-4}	7.23	1311	1.38		4.32×10^{-4}	6.14	2317	1.63	
1.48×10^{-3}	7.19	677.4	1.39		1.66×10^{-3}	6.74	600.9	1.48	
C. Vegetable-tanned leather at p_H 3.8.					D. Vegetable-tanned leather at p_H 4.3.				
1.44×10^{-4}	3.70	8772	2.70		3.98×10^{-5}	3.87	25140	2.58	
4.46×10^{-4}	6.10	2240	1.64	9.43	6.97×10^{-5}	5.40	14350	1.85	
1.43×10^{-3}	8.72	693.3	1.15		5.60×10^{-4}	9.70	1784	1.05	11.78
3.04×10^{-3}	8.90	328.9	1.12		1.74×10^{-3}	11.69	573.7	0.855	
					3.44×10^{-3}	11.74	290.7	0.855	
E. Formaldehyde-tanned leather at p_H 6.7.					F. Formaldehyde-tanned leather at p_H 7.4.				
4.54×10^{-4}	2.41	2200	4.15		4.16×10^{-4}	3.41	2406	2.93	
6.17×10^{-4}	2.74	1620	3.65	4.61	5.97×10^{-4}	3.98	1675	2.51	7.14
1.00×10^{-3}	3.48	997.8	2.87		1.18×10^{-3}	5.57	850	1.79	

It will be seen that for a particular membrane at a constant p_H, the observed potential ζ_a increases with K, and approaches a limiting value when the specific conductivity is above 1×10^{-3} mho/cm.

DISCUSSION

Previous experimental work on the electrokinetic behaviour of proteins, cellulose etc. dealt mainly with the effect of ionic strength on the cataphoretic mobility or the ζ_a potential. While an increase in the value of the ζ_a potential has been obtained with cellulose (Briggs, *J. Phys. Chem.*, 1928, **32**, 641) at very low concentrations of salts like NaCl, the result is not conclusive in the case of proteins.

Bikerman and also Rutgers (*loc. cit.*) suggested that the rise in ζ_a at low electrolyte concentration was spurious and was due to surface conductivity effect. Ghosh and

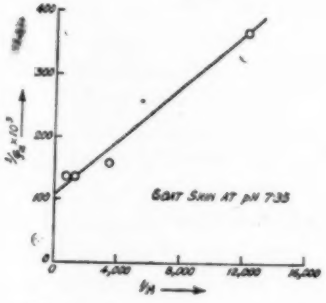
Ghosh (this *Journal*, 1954, **31**, 649) have shown that the published data on the streaming potential and surface conductivity of diaphragms constituted of cellulose fibres are again well represented by an equation of the type :

$$1/\zeta_a = 1/\zeta + \alpha \frac{K_p - K}{K} \qquad \ldots \qquad \ldots \quad (2)$$

where α is a constant, K_p, the specific conductivity of the solution inside the diaphragm and K, its bulk specific conductivity. The constant α varies for different diaphargms, depending upon the evenness and tightness of packing and specific volumes of the materials.

Diaphragms of leather or hide, having a compact weaving of fibres not destroyed by handling, are therefore very suitable for electro-osmotic measurements, since α does not change during experimentation. If within a small range of electrolyte concentration at the same p_H, the true ζ-potential and surface conductance are assumed constant, for a particular membrane, the equation (2) for surface conductance assumes the form of equation (1), referred to already, so that a plot of $1/\zeta_a$ against $1/K$ should be a straight line, the intercept of which on the $1/\zeta_a$ axis should give the value of true ζ at that p_H.

FIG. 1



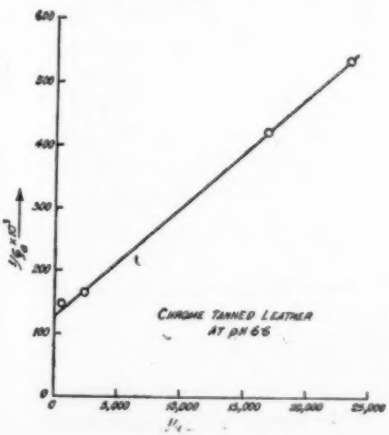
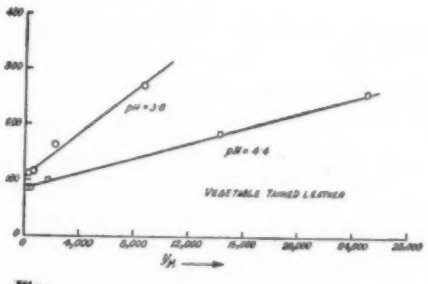


FIG. 2

FIG. 3



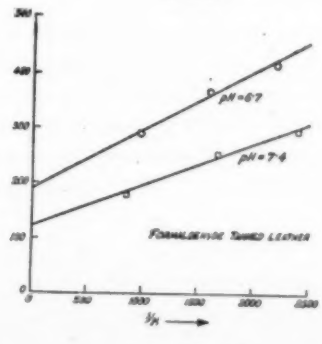


FIG. 4

Figures 1-4 show that such a linear relation has been obtained in nearly all the cases investigated. The true ζ at each p_H has been given in the last column of the table (A-F).

From the table we see that the true values of ζ differs widely from the observed values of ζ_a. However, the effect of surface conductivity becomes small when the bulk conductivity of the solution is above 10^{-3} mho/cm, as can be seen from the table.

It is to be noted that the linear relationship envisaged in equation (1) holds only so long as true ζ and the specific conductance remain constant at a given p_H, even on the addition of NaCl. These two conditions are evidently fulfilled when the concentration of NaCl added is small.

The method of evaluating true ζ developed in this paper may be utilised for the determination of isoelectric point of structured hide or leather.

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Corrigendum

(Sept. issue, 1958)

Page 675, Line 21 Read 5.6×10^9 for 5.6.

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STUDY OF COMPLEX IONS IN SOLUTION BY THE METHOD OF THERMOMETRIC TITRATION

By Kumar Krishna Chatterji

The older graphical method of representing the thermometric data has been modified by introducing a correction for the heat change due to dilution during the course of titration. Some anomalous results recorded in the literature have also been explained with the help of this modification.

In the previous communications (Chatterji, this *Journal*, 1955, **32**, 366; *1958, **35**, 57; Chatterji and Ghosh, *ibid.*, 1957, **34**, 407) the author has shown that a correction factor due to dilution must be introduced to get the actual heat changes taking place in thermometric titrations involving precipitation and acid-base neutralisation reactions. The plot of the computed values of the visual thermal changes against the volume of the titrant gives curves showing more accurate end-points than those obtained by the older method of plotting. In the present paper the same method of plotting has been recommended in the study of complex-ion formation in solution by thermometric titration. Certain anomalous results recorded in the literature can be easily explained by this means. Two such cases have been discussed here to illustrate the situation and the advantages of using the modification proposed by the author.

Halder (*ibid.*, 1946, **23**, 205) measured the heat changes arising from mixing solutions of $CdSO_4$ and KI in different concentrations and obtained breaks in the heat change—composition curves, indicating reactions between Cd^{2+} and I^- ions when these were present in the molar ratios 1:1, 1:3, 1:4 and 1:5 respectively. In fact, the occurrence of reactions in the ratios 1:1, 1:3 and 1:5 is difficult to explain and is not supported by other methods of study.

Purakayastha (*ibid.*, 1947, **24**, 257) employing the same method has indicated the stepwise formation of the complex ions $[BeF_3]^{1-}$, $[BeF_4]^{2-}$, $[BeF_5]^{3-}$ and $[BeF_6]^{4-}$ in the interaction between BeF_2 and NH_4F. Here also the existence of the last three ions lacks further evidence.

In both of the above mentioned cases, no allowance was, however, made for the dilution of the solution taken in the Dewar flask during titration, and the observed temperature changes were directly plotted against the volume of the titrant to get the thermometric curves. It is highly probable that the dilution factor alone can account for some of the breaks in the titration curves of the foregoing workers. In that case, doubtful breaks should disappear if the corrected temperature changes, ΔT_{Cv} are plotted against the volume of the titre added. As before

$$\Delta T_{Cv} = \frac{\Delta T\,(V + dv)}{V},$$

where ΔT = the observed temperature changes in °C, V = original volume in c.c. of the solution taken in the Dewar vessel, and dv = volume of the titre added in c.c.

* In the January issue of 1958, in the paper by Chatterji, the following corrections are to be made. In Table IV (p. 60), figures under columns 2 and 3 refer to % and not to g., as printed.

The plots of ΔT and ΔT_{Cv} respectively against the volume of the titre in the cases discused above, are shown in Figs. 1 and 2.

According to Halder (*loc.cit.*), the break at $Cd^{2+} : I^- = 1:1$ is due to the reaction

$$4\ CdSO_4 + 4\ KI = 2\ K_2Cd(SO_4)_2 + Cd(CdI_4).$$

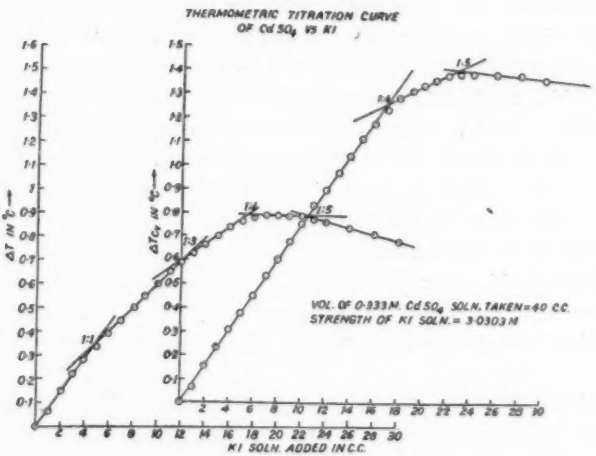
The second break at $Cd^{2+} : I^- = 1:3$ has been explained as due to the simultaneous formation of $Cd(CdI_4)$ and $K_2Cd\ I_4$ in solution.

No other evidence has been provided by Halder as to the formation of $K_2Cd(SO_4)_2$ in solution.

So far as the second break is concerned, a more plausible explanation would have been to ascribe it to the formation of the ion $[CdI_3]^-$, but Halder failed to get any indication of its formation by the thermometric titration of CdI_2 with KI.

In the corrected temperature curve (Fig. 1) the breaks at $Cd^{2+} : I^- = 1:1$, and $1:3$ are no longer shown, but the break at $Cd^{2+} : I^- = 1:4$ is clearly shown, which indicates that the ion $[CdI_4]^{2-}$ exists as a stable species in solution.

FIG. 1

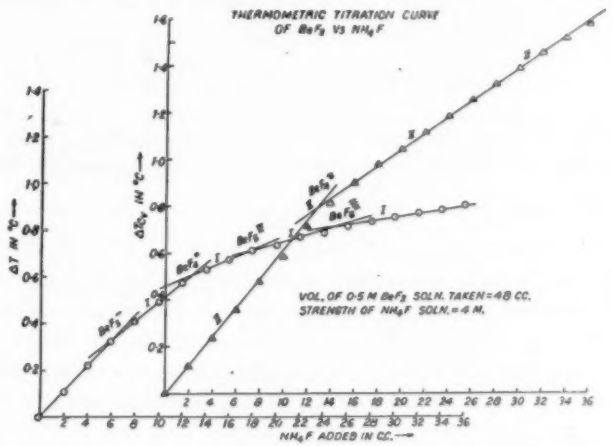

THERMOMETRIC TITRATION CURVE
OF CdSO4 VS KI
VOL. OF 0·933 M. CdSO4 SOLN. TAKEN=40 C.C.
STRENGTH OF KI SOLN.= 3·0303 M
KI SOLN. ADDED IN C.C.

The last break at $1:5$, which occurs in both the curves, possibly does not indicate any true reacting proportion of Cd^{2+} and I^-. The heat changes after the formation of $[CdI_4]^{2-}$ is also very small. The downward trend of the curve is obviously due to the fall in the temperature of the mixture in absence of any reaction, the titre added being at a lower temperature than that of the system in the Dewar.

The effect of volume correction on the thermometric curve of Purakayastha (*loc.cit.* is even more exemplary (Fig. 2). Only one reaction is indicated, the reacting proportion of $Be^{2+} : F^-$ being $1:4$. Thus, the only ion which is stabilised in solution is $[BeF_4]^2$

The other complexes suggested by Purakayastha thus have their origin in the wrong method of representation of the thermometric data.

FIG. 2



The author's best thanks are due to Prof. B. N. Ghosh, D.Sc., F.N.I., Palit Professor of Chemistry, University College of Science, for his kind interest and helpful suggestions.

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COMPOUNDS OF ANTIMONY TRICHLORIDE WITH PHENOLS AND NITROPHENOLS

By Sarju Prasad and Suresh Kumar

Several compounds of antimony have been prepared by refluxing a mixture of antimony trichloride and a phenol or a nitrophenol in organic solvents, their properties studied and their structures discussed.

The reaction of antimony trichloride with water results in the formation of antimony oxychloride, which shows that one of the chlorine atoms is differently and more stably attached to antimony than the remaining two, which are detached from the molecule. A review of literature shows that similar behaviour has been observed in the reaction between antimony trichloride and phenols, when only two chlorine atoms are replaced by the mobile hydrogen atoms of the hydroxy groups of the phenol, the remaining one remaining intact.

Causse (*Compt. rend.*, 1897, **125**, 954) obtained antimony catechol chloride by the action of catechol on an aqueous solution of antimony trichloride. Certain other phenols yielded similar derivatives, which were amorphous and readily dissociated by cold alcohol.

The present investigation was therefore undertaken with a view to studying the preparation and properties of compounds obtained by the action of phenol or nitrophenol on antimony trichloride in organic solvents.

Experimental

The phenols and nitrophenols used were of B.D.H. or Merck's "Pure" and antimony trichloride of "Extra pure" quality. The solvents were dehydrated and redistilled.

Antimony trichloride and phenol or nitrophenol solutions in organic solvents were mixed in certain molar ratio, depending upon the number of hydroxy groups present in the phenol. It was refluxed on an oil-bath till the evolution of hydrogen chloride had ceased. The compound formed was extracted with a suitable solvent to remove the excess of the reactants, dried and analysed. Two sets of experiments, taking in one antimony trichloride and in the other phenol or nitrophenol in excess, were carried out simultaneously. The results reported are an average of the two values.

Antimony was estimated as Sb_2S_3, chlorine as AgCl and the organic matter, found by difference.

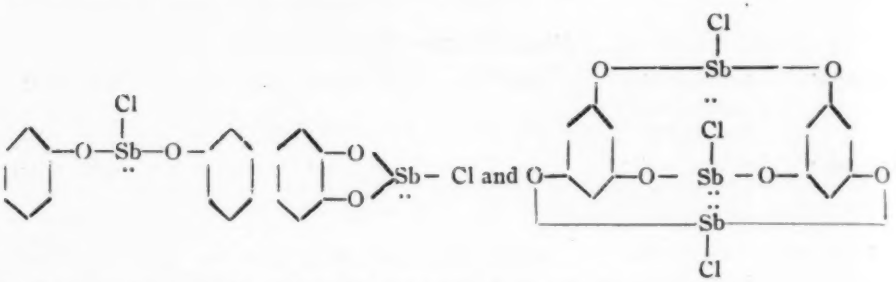
TABLE I

Phenols.	Compounds formed.	Colour.	M.P.	%Antimony. Found.	Calc.	%Chlorine. Found	Calc.	% Org. matter. Found.	Calc.
			Monohydroxy phenols.						
α-Naphthol	Antimony di-α-naphthol chloride. $SbCl(C_{10}H_7O)_2$.	Light blue	80°	27.64	27.46	8.24	8.01	64.12	64.53
β-Naphthol	Antimony di-β-naphthol chloride. $SbCl(C_{10}H_7O)_2$.	Pink	78°	27.16	27.46	7.98	8.01	64.86	64.53
Hydroquinone	Antimony di-hydroquinone chloride. $SbCl(C_6H_4OCH_3O)_2$.	Orange-yellow	160°	30.13	30.19	8.71	8.80	61.16	61.01
			Dihydroxyphenols.						
Phenolphthalein	Antimony phenolphthalein chloride. $SbCl.C_6H_4(CO)_2.(C_6H_4O)_2$.	Dirty white	230°	25.67	25.72	7.55	7.50	66.78	66.78
Resorcinol	Antimony resorcinol chloride. $SbCl(C_6H_4O_2)$.	Red-brown	103°	46.05	45.90	13.26	13.38	40.69	40.72
			Trihydroxyphenols.						
Pyrogallol	Tri-antimony di-pyrogallol chloride. $3\,SbCl(C_6H_3O_3)_2$.	Brownish pink	240° (decomp.)	53.16	53.26	15.43	15.53	31.41	31.21
Phloroglucinol	Tri-antimony di-phloroglucinol chloride. $3\,SbCl(C_6H_3O_3)_2$.	Brown-black	85° (decomp.)	53.18	53.26	15.49	15.53	31.33	31.21
			Nitrophenols.						
m-Nitrophenol	Antimony di-*m* nitrophenol chloride. $SbCl(C_6H_4NO_2.O)_2$.	Dirty powder	114°	28.22	28.10	8.15	8.19	63.63	63.71
p- ,,	Antimony di-*p*-nitrophenol chloride. $SbCl(C_6H_4NO_2.O)_2$.	Yellowish	130°	27.98	28.10	8.10	8.19	63.90	63.71
2 : 4 Di- ,,	Antimony di-2 : 4-dinitrophenol chloride. $SbCl(C_6H_3NO_2.NO_2.O)_2$.	Yellow powder	100°	23.34	23.26	6.59	6.78	70.07	69.96

DISCUSSION

From the results it is evident that one molecule of antimony trichloride reacts with two molecules of a monohydroxy and one molecule of a dihydroxy phenol and three molecules of antimony trichloride react with 2 molecules of a

trihydroxy phenol. Nitro- and dinitrophenols give similar results, only the hydroxy group being affected. The compounds formed can be represented as:



in the case of mono-, di- and trihydroxy phenols respectively.

The compounds have low melting points and are soluble in most of the organic solvents. On boiling with water or sodium hydroxide, antimony oxychloride and the respective phenol or sodium phenate are formed.

$$SbCl(PhO)_2 + H_2O = 2\ PhOH + SbOCl$$
$$SbCl(PhO)_2 + 2NaOH = 2PhONa + SbOCl + H_2O$$

The stability of these derivatives towards water, sodium hydroxide and mineral acids is as dihydroxy phenol > monohydroxy phenol > trihydroxy phenol.

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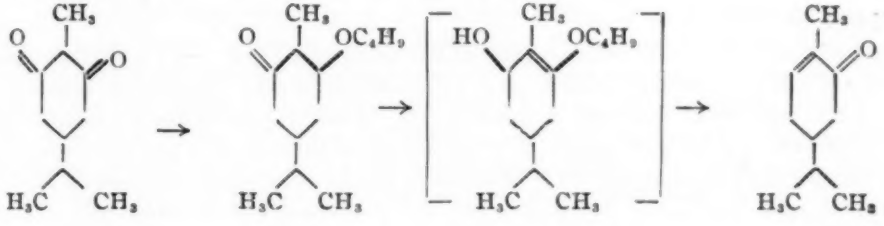
TERPENODIS. PART IV. A NEW SYNTHESIS OF *dl*-CARVOTANACETONE

By O. P. Vig and Mohan Singh

A new synthesis of *dl*-carvotanacetone has been achieved.

Carvotanacetone is a monocyclic terpene ketone which occurs in nature in its *dextro* form in the oils derived from *Blumea malcomii* and *Blumea criantha* (Simonsen and Rau, *J. Chem. Soc.*, 1922, **121**, 876 ; Schimmel's report, 1937, p. 8). It has also been isolated in the *dl*-form from the high boiling fraction of Thuja oil (Wallach, *Ber.*, 1893, **26**, 275, 182). On the basis of chemical evidence this natural ketone was formulated as (III).



(I) (II) (III)

The structure (III) was later confirmed by Frank and Hall (*J. Amer. Chem. Soc.*, 1950, **72**, 1645) by a direct synthesis of the *dl*-ketone through the diketone (I). We now record an alternative elegant synthesis of the racemate of the same naturally occurring ketone. The new approach is based on an earlier method developed by Frank and Hall (*loc. cit.*) for the preparation of enolic ethers from cyclic diketones.

5-*iso*Propyl-1 : 3-*cyclo*hexan-dione, the starting material in the present scheme, was prepared exactly according to Frank and Hall (*loc. cit.*). It was methylated with methyl iodide and aqueous potassium hydroxide (cf. Stetter, Kesseler and Meisel, *Ber.*, 1954, **87**, 1617). Whereas Frank *et al.* could not convert this 2-substituted diketone (I) into its enolic ether, we succeeded in doing so by using *iso*butyl alcohol in place of ethyl alcohol, which was employed by them. The *iso*butyl enolic ether (II) was then allowed to react with lithium aluminium hydride, followed by decomposition of the reduced product with dilute sulphuric acid (cf. Mukherji, Sharma and Vig, this *Journal*, 1956, **33**, 857). The ketone (III), *dl*-carvotanacetone, was formed in good yield. The identity of the synthetic product was established through its derivatives and ultraviolet spectrum.

Experimental *

5-iso*Propyl-2-methyl*-1 : 3-cyclo*hexan-dione* (I).—To a solution of 5-*iso*propyl-1 : 3-*cyclo*hexan-dione (15.4 g., 0.1*M* ; Frank *et al.*, *loc. cit.*) in aqueous potash (5.6 g., 0.1*M*,

* Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

dissolved in 30 c.c. of water) was added dropwise, with stirring, methyl iodide (25 g.) at ordinary temperature. The mixture was stirred for 3 hours and then extracted with ether. The ethereal layer was extracted with 10% aqueous sodium bicarbonate solution several times. The bicarbonate solution was acidified with HCl and the resulting precipitate was recrystallised from aqueous acetone, yield 10 g. (60%), m.p 179 81°. Frank and Hall (*loc.cit.*) reported m.p. 178-81°.

2-*Methyl*-3-iso*butoxy*-5-iso*propyl*-2-cyclo*hexenone* (II).—A mixture of the diketone (I, 16.8 g.), *iso*butyl alcohol (30 g.), dry benzene (200 c.c.) and *p*-toluenesulphonic acid (200 mg.) was refluxed under a modified Dean and Stark apparatus. It was heated for 5 hours in an oil-bath and when no more water separated, it was cooled. The free acid in the mixture was neutralised with sodium ethoxide and then it was diluted with water. The benzene layer was separated and the aqueous portion was extracted with ether. The combined extract was washed with water and dried over sodium sulphate. It was stripped off the solvent and the residue distilled under vacuum, b.p. 145-50°/5 mm, yield 14 g. (62%), n_D^{15} 1.486. (Found: C, 74.82; H, 10.62. $C_{14}H_{24}O_2$ requires C, 75.00; H, 10.71%).

5-iso*Propyl*-2-*methyl*-2-cyclo*hexenone* (dl-*Carvotanacetone*) (III).—To a well-stirred solution of lithium aluminium hydride (0.95 g.) in anhydrous ether (100 c.c.) at ordinary temperature was added dropwise a solution of 2-methyl-3-*iso*butoxy-5-*iso*propyl-2-*cyclo*hexenone (11.2 g.) in ether (50 c.c.) at such a rate as to maintain a gentle refluxing. The mixture was stirred for half an hour after the addition and then decomposed with 10 c.c. of 10% H_2SO_4. It was kept as such for 2 hours and then extracted with ether. The ethereal layer was washed with water and dried over anhydrous sodium sulphate. The solvent was removed and the product distilled under reduced pressure, b. p. 98-100°/7 mm, yield 6.2 g. (80%), n_D^{20} 1.4790 (Brühl, *Ber.*, 1899, **32**, 1225, reported n_D^{20} 1.4805); λ_{max}^{alc} 235 mμ (log ε 4.14) (Frank *et al.*, *loc. cit.*, report for dl-carvotanacetone λ_{max}^{alc} 237 mμ; log ε 4.19). (Found: C, 78.58; H, 10.34. Calc. for $C_{10}H_{16}O$: C, 78.89; H, 10.59%).

The *semicarbazone*, prepared in the usual way and crystallised from alcohol, melted at 178° (Baeyer, *Ber.*, 1894, **27**, 1923, recorded m.p. 177-79° for *dl*-carvotanacetone derivative). (Found: N, 19.87. Calc. for $C_{11}H_{19}ON_3$: N, 20.08%).

The 2:4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method and crystallised as red micro-crystals from ethyl acetate, m.p. 191° (Short and Read, *J. Chem. Soc.*, 1939, 1044, reported for *dl*-carvotanacetone 2:4-dinitrophenylhydrazone, m.p. 191-92°). (Found: N, 16.59. Calc. for $C_{16}H_{20}O_4N_4$: N, 16.85%).

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PREPARATION OF ARYLAMIDES OF 2-METHOXY-, 4-METHOXY- AND 2-HYDROXY- 4-METHOXY-BENZOIC ACIDS

D. M. PHATAK AND G. V. JADHAV*

Several arylamides of 2-methoxy-,4-methoxy- and 2-hydroxy-4-methoxy-benzoic acids have been prepared by condensing the acid chloride with the amines in presence of pyridine or PCl_3.

A few arylamides of 2-hydroxy-4-methoxybenzoic acid, and of 2- and 4-methoxybenzoic acids have been prepared by the interaction of the acid and the amine in presence of phosphorus trichloride or pyridine.

EXPERIMENTAL

2-Methoxybenzoyl chloride was prepared by boiling the acid (10 g.) in dry toluene (30 c.c.) with thionyl chloride (10 c.c.) for about 8 hours and removing toluene and excess of thionyl chloride by distillation. The crude acid chloride was mixed with the requisite amine (12 g.) in presence of pyridine (10 c.c.), and the mixture was left over at room temperature for about 15 minutes. The mixture was then first triturated with HCl (dilute) and then with a dilute solution of NaOH. The compounds obtained were crystallised from suitable solvents in yields of nearly 65% (Table I).

TABLE I

[A represents 2-methoxybenz-]

Amides.	Cryst. from.	Cryst. appearance.	M. P.	Formula.	%Nitrogen. Found.	Calc.
* A-anilide	Chloroform + pet. ether	Colorless needles	74-75°	$C_{14}H_{13}O_2N$	6.3	6.2
A-*o*-toluidide	EtOH	,, plates	89-90°	$C_{15}H_{15}O_2N$	5.8	5.8
A-*m*- ,,	Dil. alcohol	,, needles	74-75°	,,	6.0	5.8
A-*p*- ,,	Do	Do	62-66° (distils at 205-206°/ 0.75 mm)	,,	6.1	5.8
A-*o*-nitroanilide	Acetic acid	Pale yellow needles	133-34°	$C_{14}H_{12}O_4N_2$	10.6	10.3
A-*m*- ,,	Benzene	Do	139-40°	,,	10.0	10.3
A-*p*- ,,	Acetic acid	Yellow soft needles	170-71°	,,	10.2	10.3
A-*p*-anisidide	Dil. EtOH	Colorless prisms	73-74°	$C_{15}H_{15}O_3N$	5.7	5.5
A-*p*-phenetidide	EtOH	,, rect. plates	94-95°	$C_{16}H_{17}O_3N$	5.5	5.2

* It was prepared by Haller (*Compt. rend*, 1895, **121**, 189; Beilstein, XII, p. 501) by heating the acid with phenyl *iso*cyanate. He recorded m.p. 62°.

The arylamides of 4-methoxybenzoic acid were prepared in the same way as those of 2-methoxy isomer (Table II). The yields were about 65%.

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TABLE II

[B represents 4-methoxybenz-]

Amides.	Cryst. from.	Cryst. appearance.	M.P.	Formula	%Nitrogen. Found.	Calc.
B-*o*-toluidide	EtOH	Colorless needles	161-62°	$C_{15}H_{15}O_2N$	6.0	5.8
B-*m*- ,,	Dil. EtOH	Do	107-108°	,,	6.0	5.8
B-*p*- ,,	Acetic acid	,, rect. plates	153-54°	,,	6.1	5.8
B-*o*-nitroanilide	Benzene+pet. ether	Yellow needles	114-15°	$C_{14}H_{12}O_4N_2$	10.5	10.3
B-*o*-anisidide	dil. MeOH	Colorless needles	95-96°	$C_{15}H_{15}O_3N$	5.8	5.5
* B-*p*- ,,	EtOH	,, leaflets	202-203°	,,	5.5	5.5
B-*p*-phenetidide	Acetic acid	,, needles	174-75°	$C_{16}H_{17}O_3N$	5.5	5.2
† B-β-naphthyl-amide	Benzene	,, ,,	179-80°	$C_{18}H_{15}O_2N$	5.3	5.0

* Schnackeneberg and Scholl (*Ber.*, 1903, **36**, 654) prepared this compound by Beckmann's transformation.

† The crude product was washed with dilute acetic acid instead of dilute hydrochloric acid as in other cases.

The amides of 2-hydroxy-4-methoxybenzoic acid were prepared by heating on a boiling water-bath for 4 hours the acid (5 g.) with the amine (10 g) in presence of phosphorous trichloride (1.5 c.c.) and then diluting the mixture and working up the product in the same way as in the previous two cases, the only difference being that sodium bicarbonate was used in place of sodium hydroxide. These are described in Table III. The yields were about 30%.

TABLE III

[C represents 2-hydroxy-4-methoxybenz-]

Amides.	Cryst. from.	Cryst. appearance.	M. P.	Formula.	%Nitrogen. Found.	Calc.
C-anilide	EtOH	Colorless granules	157-58°	$C_{14}H_{13}O_3N$	6.0	5.8
C-*o*-toluidide	,,	,, needles	143-44°	$C_{15}H_{15}O_3N$	5.7	5.4
C-*m*- ,,	,,	,, ,,	141-42°	,,	5.3	5.4
C-*p*- ,,	Benzene	,, rhombic plates	151-52°	,,	5.5	5.4
C-*o*-nitroanilide	Acetic acid	Yellow needles	144-45°	$C_{14}H_{12}O_5N_2$	9.6	9.7
C-*m*- ,,	,,	Colorless needles	194-95°	,,	10.0	9.7
C-*p*- ,,	,,	Pale yellow plates	223-24°	,,	9.8	9.7
* C-*o*-anisidide	Dil. MeOH	Colorless needles	100-101°	$C_{15}H_{15}O_4N$	5.3	5.1
C-*p*- ,,	Acetic acid	,, ,,	164-65°	,,	5.2	5.1
C-*p*-phenetidide	Chloroform+pet. ether	,, lustrous cubes	151-52°	$C_{16}H_{17}O_4N$	4.8	4.9
† C-β-naphthylamide	Benzene	,, cubes	174-75°	$C_{18}H_{15}O_3N$	4.9	4.8

* The reaction mixture in this case was heated at 120° to get the product in better yields.

† The crude product was washed with dilute acetic acid instead of dil. HCl as in other cases.

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COMPOUNDS OF MANGANOUS CHLORIDE WITH HETEROCYCLIC BASES AND SECONDARY AND TERTIARY AMINES

By Sarju Prasad and Kamta Prasad Kacker

The complex compounds of manganese have been prepared by the action of manganous chloride on some heterocyclic bases and secondary and tertiary amines in alcoholic medium.

Reitzenstein (*Z. anorg. Chem.*, 1898, **18**, 253) prepared dipyridino-manganous chloride, $MnCl_2.(C_5H_5N)_2$, and diquinolino-manganous chloride, $MnCl_2.(C_9H_7N)_2$, by adding an excess of pyridine or quinoline respectively to a solution of manganous chloride in alcohol. Hayes (*J. Amer. Chem. Soc.*, 1902, **24**, 360) obtained the compound, $C_5H_5N.MnCl_2.HCl$, by adding a solution of $MnCl_2$ in HCl to a solution of pyridine hydrochloride. Dubsky and Dostal (Pub. faculte Sci. Univ. Masaryk, No. 196, 17-23, 1934) studied the formation of quinoline (Q) complexes : (*i*) $MnCl_2(Q)_2.3H_2O$, and (*ii*) $(MnCl_4)H_2(Q)_2.2H_2O$. Sacconi (*Ann. Chim. Rome*, **40**, 386, 150) obtained with nicotinamide (NA), the complex compound, $MnCl_2.2(NA)$. It is evident that very little work has been done on the formation of compounds of manganous chloride with heterocyclic bases, and no work has been done on the formation of compounds with secondary and tertiary amines. The present investigation was therefore undertaken with a view to studying the preparation and properties of these compounds.

Experimental

The heterocyclic bases and amines used were of B.D.H. 'Pure' quality and alcohol was dehydrated and redistilled. Manganous chloride was dehydrated by passing HCl gas over hydrated manganous chloride at 160°.

Manganous chloride and the organic substances were dissolved separately in alcohol and the compounds were prepared by two methods. In the first case, the organic substance was added to the manganous chloride solution slowly, with constant stirring, till it was in slight excess. In the second case, the manganous chloride solution was added to the organic compound till it was in slight excess. If a precipitate was not obtained in either of the cases, the solution was evaporated slowly on a sand-bath, when the compound separated out. It was kept for about an hour, filtered, washed with alcohol, dried at low temperatures and analysed.

Manganese was estimated as $Mn_2P_2O_7$ and chlorine as AgCl. Alcohol of crystallisation was estimated by heating the substance to a constant weight at 100° and noting down the loss in weight. The organic substance was found by difference.

TABLE I

Manganous chloride-heterocyclic bases.

Base.	Compound formed.	Colour.	%Manganese. Found.	%Manganese. Calc.	%Chlorine. Found.	%Chlorine. Calc.	%Org. matter. Found.	%Org. matter. Calc.
Piperidine	Mono-piperidino-M * $MnCl_2.C_5H_{11}N$.	Dark brown	27.25	26.05	33.46	33.64	39.29	40.31
Quinoline	Mono quinolino-M $MnCl_2.C_9H_7N$.	Light brown	20.59	21.55	26.75	27.83	52.66	50.62
γ-Picoline	Mono-alcoholo-mono-γ-picolino-M $MnCl_2.C_6H_7N.C_2H_5OH$	Light rosy [Alcohol(%) : Found 17.10; Calc. 17.37]	20.48	20.73	26.62	26.77	35.80	35.13
Piperazine	Mono-piperazino-di-M $2MnCl_2.(C_4H_{19}N_2)$	Dark brown	33.54	32.53	42.38	42.01	24.08	25.46
Nicotine	Mono-nicotino-di-M $2MnCl_2.(C_{10}H_{14}N_2)$	White	26.13	26.16	34.75	34.29	39.12	39.15

* M = Manganous chloride.

TABLE II

Manganous chloride-secondary and tertiary amines.

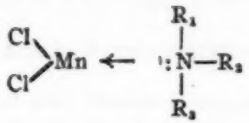
Amines.	Compound formed.	Colour	%Manganese. Found.	%Manganese. Calc.	%Chlorine. Found.	%Chlorine. Calc.	%Org. matter. Found	%Org. matter. Calc.
Dimethyl-aniline	Mono-dimethylanilino-M $MnCl_2.C_6H_5N(CH_3)_2$	Dark blue	23.19	22.25	28.39	28.73	48.42	49.02
Diethyl-aniline	Mono-diethylanilino-M $MnCl_2.C_6H_5N(C_2H_5)_2$	Grey	19.81	19.97	26.34	25.79	53.85	54.24
Dimethyl-*o*-toluidine	Mono-dimethyl-*o*-toluidino-M $MnCl_2.CH_3C_6H_4N(CH_3)_2$	Do	20.52	21.05	27.61	27.18	51.87	51.77
Dimethyl-*p*-toluidine	Mono-dimethyl-*p*-toluidino-M $MnCl_2.CH_3C_6H_4N(CH_3)_2$	Brick-red	20.49	21.05	28.43	27.18	51.08	51.77
Triethyl-amine	Mono-triethylamino-M $MnCl_2.(C_2H_5)_3N$	White	23.64	24.19	32.17	31.24	44.19	44.57
Dibenzyl-amine	Mono-dibenzylamino-M $MnCl_2.(C_6H_5CH_2)_2NH$	Brown	16.39	17.01	22.69	21.97	60.92	61.02
Tribenzyl-amine	Mono-tribenzylamino-M $MnCl_2.(C_6H_5CH_2)_3N$	White	14.07	13.30	18.06	17.18	67.87	69.52

M = Manganous chloride.

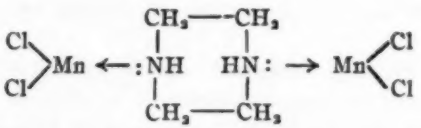
DISCUSSION

Manganese being a transitional element, should exhibit a tendency to form complex compounds readily, but the same is lowered considerably when it is in divalent state. The tendency is further depressed in the case of secondary and tertiary amines due

to weak co-ordinating power of the nitrogen atom with the result that unstable compounds, in which the ratio of $MnCl_2$: amine = 1 : 1 are formed. The instability of the compounds is probably due to the fact that neither the E. A. N. assumes the inert gas configuration nor there is any symmetry in the structure :



All the compounds with heterocyclic bases are stable except that obtained with nicotine, which is unstable and turns black and is rendered viscous on exposure to atmosphere. The compound with piperazine, which is fairly stable, can be represented as :



All the compounds hydrolyse readily on boiling with water and are decomposed by mineral acids. These do not give a sharp melting point and probably decompose when heated at a high temperature. When heated with sodalime, the liquid base separates out.

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COMPOUNDS OF MANGANOUS CHLORIDE WITH MONO- AND DI-AMINES

By Sarju Prasad and V. Rama Reddy

Several complex compounds of manganous chloride have been prepared by the action of mono- and di-amines on manganous chloride in organic solvents, their properties studied and structures discussed.

Rose (*Pogg. Ann.*, 1830, **20**, 148) reported the formation of hexammino manganous chloride, $Mn(NH_3)_6.Cl_2$, by passing dry ammonia gas over anhydrous manganous chloride at low temperatures. The compound on heating lost ammonia, forming the diammine, $Mn(NH_3)_2.Cl_2$.

Feldt (*Ber.*, 1894, **27**, 405) prepared dihydroxylamino manganous chloride, $Mn(NH_2OH)_2.Cl_2$, by treating hot aqueous solution of manganous chloride with hydroxylamine hydrochloride and adding a further quantity of the base in alcohol.

Leeds (*J. Amer. Chem. Soc.*, 1888, **3**, 112) obtained dianilino manganous chloride, $Mn(C_6H_5NH_2)_2.Cl_2$, by adding an excess of aniline to a solution of manganous chloride in alcohol.

Biltz and Huttig (*Z. anorg. Chem.*, 1919, **109**, 89) determined the dissociation pressure and curves of various ammonium derivatives of manganous chloride. Anhydrous $MnCl_2$ absorbs ammonia gas at the temperatures of solid CO_2 and alcohol to form the hexammine, $MnCl_2.6NH_3$. At 76.5° the isothermal falls a little and then remains horizontal until the composition falls to that of the diammine. The isothermal for the equilibrium,

$$MnCl_2.2NH_3 \rightleftharpoons MnCl_2.NH_3 + NH_3 \rightleftharpoons MnCl_2 + 2NH_3,$$

has been determined at 229° and indicates the existence of the mono-ammine.

Zvyagintsev and Gruzinskogo (*Ind. Inst. Inn. Kisova*, 1939, **11**, 79; *Khiur Referat Z.*, 1940, **12**, 15) obtained the compound, $MnCl_2.(CH_2NH_2)_2.2HCl.H_2O$, by treating the concentrated manganous chloride solution with HCl and adding ethylenediamine.

As very few compounds of manganous chloride with mono- and di-amines are reported in the literature, the present investigation has been undertaken with a view to studying the preparation and properties of some of them.

Experimental

The amines and manganous chloride used were of B.D.H. or Merck's 'Pure' quality, and alcohol and benzene were dehydrated and redistilled.

Anhydrous manganous chloride was prepared by passing dry HCl gas over hydrated manganous chloride at 150-60°.

Manganous chloride was dissolved in alcohol and the respective amine in benzene separately. An excess of the organic component was added to the manganous chloride

solution till the precipitation was complete. In cases where the precipitate was not obtained on mixing the solutions, it was evaporated slowly on a sand-bath when the compound separated out. The precipitate was separated by filtration, washed free of the amine and dried at the room temperature.

Manganese was estimated as $Mn_2P_2O_7$ and chlorine as AgCl. Solvent of crystallisation was estimated by heating the substance to a constant weight and noting down the loss in weight. The organic matter was found by difference.

TABLE I

Manganous chloride with mono- and diamines.

[$MnCl_2$: amino group = 1 : 2].

Amines.	Compounds formed.	Colour.	% Manganese. Found.	Calc.	% Chlorine Found.	Calc.	% Org. matter. Found.	Calc.
α-Naphthyl-amine	Di-α-naphthylamino-M* $MnCl_2.(\alpha\text{-}C_{10}H_7NH_2)_2$	White	12.84	13.32	18.05	17.20	69.11	69.48
β-Naphthyl-amine	Di-β-naphthylamino-M $MnCl_2.(\beta\text{-}C_{10}H_7NH_2)_2$	Violet	13.63	13.32	17.79	17.20	68.58	69.48
p-Toluidine	Di-*p*-toluidino-M $MnCl_2.(p\text{-}C_6H_4CH_3NH_2)_2$	White	15.60	16.15	20.59	20.84	63.81	63.03
Phenyl-hydrazine	Diphenylhydrazino-M $MnCl_2.(C_6H_5NH.NH_2)_2$	Brown	16.57	16.06	21.92	20.73	61.51	63.21
Ethylene-diamine	Mono-ethylenediamino-M $MnCl_2.(NH_2CH_2.CH_2NH_2)$	Grey	28.08	29.54	37.77	38.15	34.15	32.31
p-Phenylene-diamine	Mono-*p* phenylenediamino-M $MnCl_2.[p\text{-}C_6H_4(NH_2)_2]$	Dark violet	23.12	23.47	29.68	30.31	47.20	46.22
o-Phenylene-diamine	Mono-*o*-phenylene-diamino-M $MnCl_2.[o\text{-}C_6H_4(NH_2)_2]$	Greenish white	23.85	23.47	30.81	30.31	45.34	46.22
Benzidine	Mono-benzidino-M $MnCl_2.(NH_2C_6H_4.C_6H_4NH_2)$	Do	17.12	17.71	23.47	21.87	59.41	60.42
o-Dianisidine	Mono-*o*-dianisidino-M $MnCl_2.(NH_2OCH_3C_6H_3.C_6H_3CH_3ONH_2)$	Ash	15.29	14.85	19.54	19.16	65.17	65.99
o-Tolidine	Mono-*o*-tolidino-M $MnCl_2.(NH_2CH_3C_6H_3.C_6H_3CH_3NH_2)$	Dark grey	15.72	16.25	20.90	20.97	63.38	62.78

*M stands for manganous chloride.

DISCUSSION

According to Sidgwick ("Electronic Theory of Valency", 1927) the maximum covalency that should be exhibited by manganese is six, but no such compound in which it exhibits a covalency of '6' has so far been reported. The co-ordination number of manganese in all the cases studied is 4.

Cox *et al.* (*J. Chem. Soc.*, 1937, 1556) found by X-ray methods that manganous chloride dipyridine, $MnCl_2.Py_2$, was a 4-covalent compound, with four groups in a plane with the central atom and at the corners of the square. But by calculating Bohr magnetons, Mellor and Coryell (*J. Amer. Chem. Soc.*, 1938, **60**, 1786) assigned a structure of the octahedral ionic type with two shared edges for this compound.

It has been found that two molecules of a monoamine and one of a diamine combine with one molecule of manganous chloride and the compounds formed can be represented as Mn (2A).Cl_2 and Mn (D).Cl_2, where A = a monoamine and D = a diamine.

This shows that in none of them the E.A.N. assumes the inert gas stable configuration, but they have a symmetrical structure and, hence, they are stable.

All the compounds are stable in the dry atmosphere at the room temperature, but these hydrolyse readily on boiling with water. Most of them do not melt but decompose at high temperatures. On heating with sodalime, the corresponding amines separate out and condense on the cooler part of the test-tube. The diamino compounds are more stable than the monoamino derivatives, probably due to the formation of chelate compounds.

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RUBEANIC ACID AND ITS DERIVATIVES AS COLORIMETRIC REAGENTS. PART IV. *NN'*-DIBENZYL- AND *NN'*-DIPHENYL-RUBEANIC ACIDS

By J. Xavier and Privadaranjan Rây

The use of *NN'*-dibenzyl- and *NN'*-diphenyl-rubeanic acids as colorimetric reagents for certain elements of the transitional series is reported. *NN'*-Dibenzylrubeanic acid gives metallic complexes almost similar to those of the parent compound, but with lower solubilities in common organic solvents. However, the aryl derivative (*NN'*-diphenylrubeanic acid), though highly coloured, can be used with equal or even greater advantage than rubeanic acid itself for the colorimetric determination of copper, nickel, cobalt and palladium. The reagent has been found to be more sensitive than its parent compound or its alkyl analogues. For comparison, the behaviour of monothio-oxanilide towards various metallic cations has also been studied.

The effect of substitution in the amido groups of rubeanic acid by alkyl radicals in respect of the usefulness of those products as colorimetric reagents has been described in the earlier part of this series (this *Journal*, 1958, **35**, 633). In the present paper a study of similar substitution by groups containing aromatic rings has been presented. The low solubility of *NN'*-dibenzylrubeanic acid as well as of its metallic complexes in organic solvents seems to furnish an evidence of the pronounced weighting effect of the substituent. This makes the reagent unsuitable for the direct determination of metallic cations. On the other hand, *NN'*-diphenylrubeanic acid and its metallic complexes are sufficiently soluble in organic solvents to permit its use as a very suitable reagent for the spectrophotometric estimation of copper, cobalt, nickel and palladium. It is found to be more sensitive than its parent compound or its alkyl analogues. As the colour of most of the metal complexes of *NN'*-diphenylrubeanic acid can be readily extracted form their aqueous pyridine solution by *iso*butyl or *iso*-amyl alcohol, the methods of colorimetric estimation with this reagent can be further refined and made more effective by such extractions. For, it can be used for estimating concentration of metal ions much lower than what is possible of estimation in aqueous pyridine solution. Monothio-oxanilide, which is related closely to *NN'*-diphenylrubeanic acid (dithio-oxanilide), has been found, however, much less effective as a reagent for analytical purposes. The colour of its metallic compounds is rather weak and dull, besides being unstable.

Experimental

NN'-*Dibenzylrubeanic Acid* ($C_6H_5.CH_2$-NH-CS-CS-NH-$CH_2.C_6H_5$)

The compound was prepared by warming rubeanic acid with an alcoholic solution of benzylamine (Wallach and Reinhardt, *Annalen*, 1891, **262**, 354). The properties of metal-*NN'*-dibenzylrubeanates are summarised in Table I.

TABLE I

Metal.	Properties.
Copper (II)	Greenish black precipitate (from neutral, ammoniacal or weakly acetic acid solution); very difficultly soluble in most of the common organic solvents.
Cobalt (II)	Deep brown precipitate with a yellow tinge (from ammoniacal solution); somewhat soluble in pyridine, but very sparingly soluble in other organic solvents. The orange-yellow pyridine solution is extractable by toluene.
Nickel (II)	Deep violet-pink precipitate (from ammoniacal solution); fairly soluble in acetone, benzene, chloroform, ethyl or amyl acetate, *iso*amyl or *iso*butyl alcohol and more easily in pyridine (deep violet colour, extractable by *iso*amyl or *iso*butyl alcohol, ethyl or amyl acetate, toluene or chloroform). But the pyridine solution is unstable, turning turbid in a short time.
Palladium (II)	Orange-yellow precipitate (from ammoniacal solution); soluble in acetone, chloroform, ethyl or amyl acetate and pyridine (yellow colour, extractable by toluene, benzene, etc.). But the solution in these solvents rapidly turns turbid.
Silver (I)	Pale yellow precipitate (from neutral solution).
Gold (III)	Same as above (acid solution).
Platinum (IV)	Orange-yellow coloration (from acid solution).
Lead (II)	Yellow-white precipitate (from neutral solution).

Spot Tests.—The spot tests of copper, cobalt, nickel and palladium, using *NN'*-dibenzylrubeanic acid were carried out in a manner analogous to that with other substituted rubeanic acids (*loc. cit.*). The identification and concentration limits for different metals are recorded below:

Cu: 0.10γ $(1:5\times10^5)$. Co: 0.035γ $(1:1.4\times10^6)$.

Ni: 0.04γ $(1:1.25\times10^6)$. Pd: 0.06γ $(1:5\times10^5)$.

NN'-Diphenylrubeanic Acid (C_6H_5-NH-CS-CS-NH-C_6H_5)

NN'-Diphenylrubeanic acid was obtained along with monothio-oxanilide (C_6H_5-NH-CS-CO-NH-C_6H_5) by the action of phosphorus pentasulphide on oxanilide (Reissert, *Ber.*, 1904, **37**, 3720). Dithio-oxanilide crystallises out from glacial acetic acid as shining reddish yellow plates, m.p. 133-34°. Monothio-oxanilide forms pure yellow crystals, m.p. 144-45°.

The properties of the metallic complexes of *NN'*-diphenylrubeanic acid and monothiooxanilide are shown in Table II.

TABLE II

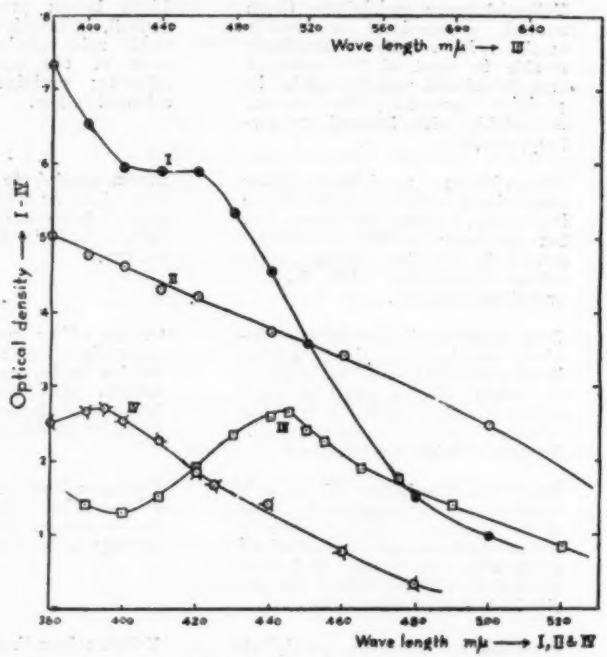
Metal.	*NN'*-Diphenylrubeanic acid (Dithio-oxanilide) (I)	Monothio-oxanilide (II)
Copper (II)	Yellowish green pricipitate (from neutral, ammoniacal or weakly acetic acid solution); sparingly soluble in most of the common organic solvents; easily soluble in pyridine (greenish yellow colour, extractable with *iso*amyl or *iso*butyl alcohol).	Light brown precipitate (from neutral, ammoniacal or weakly acetic acid solution); soluble in most of the common organic solvents; pyridine solution is coloured yellow.
Cobalt (II)	Orange-brown precipitate (from ammoniacal solution); easily soluble in benzene, toluene, chloroform, etc., but sparingly soluble in acetone; soluble in pyridine (orange-yellow colour, extractable with *iso*amyl or *iso*butyl alcohol).	Brown precipitate (from ammoniacal solution); slightly soluble in alcohol, benzene, chloroform, etc.; easily soluble in pyridine (yellow colour).
Nickel (II)	Deep violet precipitate (from ammoniacal solution); sparingly soluble in alcohol (hot), acetone, *iso*amyl or *iso*butyl alcohol, ethyl or amyl acetate; easily soluble in pyridine (pink-red colour, extractable with *iso*amyl or *iso*butyl alcohol).	Orange-yellow precipitate (from ammoniacal solution); sparingly soluble in benzene, alcohol, chloroform, etc.; easily soluble in *iso*amyl or *iso*butyl alcohol and pyridine (yellow colour).
Palladium (II)	Deep red precipitate (from acid solution); easily soluble in most of the common organic solvents; the orange-yellow pyridine solution is extractable with *iso*amyl or *iso*butyl alcohol, chloroform, carbon tetrachloride and ethyl or amyl acetate.	Orange-yellow precipitate (from acid solution); soluble in most of the common organic solvents (orange-yellow colour).
Platinum (IV)	Brownish red nsutable precipitate (from acid solution).	Yellow colour (from acid soln.).
Gold (III)	Orange-red unstable precipitate (from acid solution).	Orange-yellow colour (from acid solution).
Silver (I)	Yellow precipitate (from neutral solution); stable towards dilute acids, but dilute alkali decomposes it; slightly soluble in organic solvents.	No precipitate or colour.
Bismuth (III)	Yellow precipitate (from acid solution), changing to brown and finally black.	Do
Lead (II)	Yellow precipitate (from neutral solution), decomposed by acids.	Do
Cadmium (II)	Pale yellow precipitate (from neutral solution), decomposed by acids.	Do

Spot Tests.—A very dilute alkaline ($N/100$) solution of the reagent was used for testing copper, cobalt and nickel. Palladium was detected in slightly acid solution. Identification and concentration limits are: Cu, 0.10 γ ($0 : 10^5$); Co, 0.10 γ ($1 : 10^6$); Ni, 0.40 γ ($1 : 5 \times 10^5$) and Pd, 0.20 γ ($1 : 5 \times 10^5$).

FIG. 1

Absorption curves.

NN'-Diphenylrubeanic acid metallic complex. Cell length = 10 mm



Curve I—6 p.p.m. Cu. Curve II—1.45 p.p.m. Co. Curve III—2 p.p.m. Ni. Curve IV—2 p.p. m. Pd.

Spectrophotometric Determinations.—Based on the solubility of metal *NN'*-diphenyl rubeanates in pyridine, spectrophotometric methods of determining copper, cobalt, nickel and palladium have been developed. Copper was determined by measuring the optical density of the greenish yellow solution at 420 mμ; cobalt from the optical density of its orange-yellow colour at 410 mμ; nickel from that of its pinkish red colour at 510 mμ and palladium from that of its yellow colour at 395 mμ. The colour systems in all the cases were found to obey Beer's law.

Determination of Copper

The following solutions were used: Standard copper solution, 0.05 mg. Cu/c.c. Reagent solution, prepared by mixing equal volumes of a 0.1% alcoholic solution of *NN'*-diphenylrubeanic acid and an aqueous solution (approximately 1*N*) of sodium hydroxide. The reagent solution was used after about half an hour from its preparation. Disodium versenate solution, 1% aqueous.

Absorption maximum (in the ultraviolet region).—The optical density of the complex solution is almost constant between 410 and 420 mμ (cf. Curve I, Fig. 1). Measurements were made at 420 mμ.

Pyridine concentration: 5 c.c. of pyridine in a total volume of 25 c.c. made up with water.

Reagent concentration: Maximum colour intensity was developed by 1 c.c. of the reagent solution, when the copper concentration did not exceed 0.20 mg.

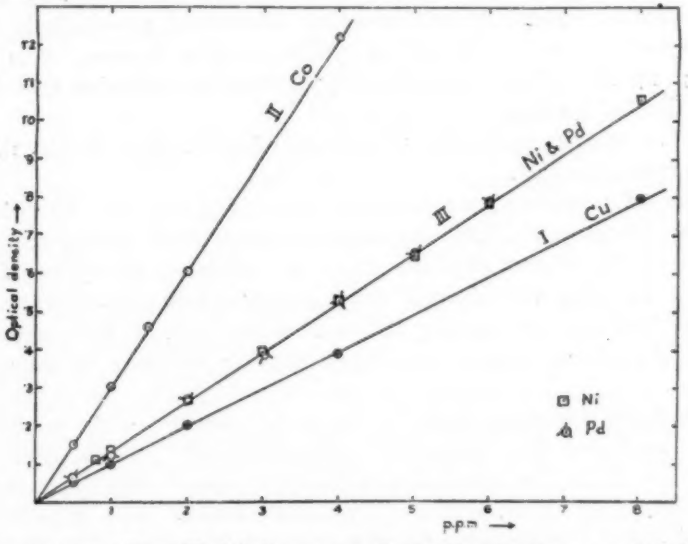
Alkali concentration: Varying amounts of sodium hydroxide (from 1 c.c. of 0.1*N* to 10 c.c. of 1*N*) solution were added after the addition of the reagent solution. It was observed that the colour intensity remained unaltered, when measured against a reagent blank containing an equal quantity of sodium hydroxide.

Beer's Law.—The system obeys Beer's law (cf. Curve I, Fig. 2).

FIG. 2

Beer's law curves.

NN'-Diphenylrubeanic acid metallic complex. Cell length = 10 mm.



Curve I—Copper; 420 mμ. Curve II—Cobalt; 410 mμ. Curve III—Nickel; 510 mμ; Palladium; 395 mμ.

Stability of the colour.—A solution containing 2 p.p.m. Cu remained clear without any appreciable change in its optical density for more than 24 hours. But when the copper content was about 10 p.p.m., a slight opalescence was noticed after 5-6 hours.

Sensitivity: 0.01 γ Cu/cm² (Sandell) and 0.08 γ Cu/cm² (practical).

Effect of diverse ions.—Cations that are precipitated, either by the alkaline reagent solution or by pyridine, interfere with the estimation of copper. However, disodium versenate (disodium salt of ethylenediaminetetra-acetic acid) has been found to be a suitable sequestering agent for many cations. The colour intensity of the copper *NN'*-diphenylrubeanate is unaffected by the addition of the versenate. The following ions were masked for 2 p.p.m. Cu by the addition of 1% aqueous solution of versenate:

Co^{2+} (50 γ), Ni^{2+} (50 γ), Pb^{2+} (500 γ), Cd^{2+} (400 γ), Cr^{3+} (100 γ), molybdate (200 γ), tungstate (200 γ) and Sn^{2+} (20 γ). Even when present in very small amounts, the following ions interfere : Fe^{2+}, Fe^{3+}, Bi^{3+}, Hg^{2+}, Mn^{2+}, Ag^{+}, Au^{3+}, Pt^{4+} and Pd^{2+}.

Procedure.—To the test solution, containing preferably less than 0.3 mg. copper, 5 c.c. pyridine and 5 c.c. of 1% aqueous solution of disodium versenate were added. The volume was roughly adjusted to 20 c.c. with distilled water and treated with 1 c.c. of the alkaline reagent solution. A greenish yellow colour developed almost instantaneously. The volume was then made up to 25 c.c. with distilled water, and the optical density of the solution was measured at 420 mμ, against a reagent blank which contained also the same amount of alkali as the sample solution.

Determination of Cobalt

The following solutions were used : Standard cobalt solution, 0.025 mg. Co/c.c. Reagent solution, prepared by mixing equal volumes of an alcoholic solution of *NN'*-diphenylrubeanic acid (0.1%) and an aqueous solution (approx. *N*/2) of sodium hydroxide ; 1% aq. sodium acetate solution, 5% (aqueous) potassium cyanide solution ; and freshly distilled pyridine.

Absorption maximum : In the ultraviolet region (cf. Curve II, Fig. 1). Measurements were made at 410 mμ.

Pyridine concentration : 5 c.c. in a total volume of 25 c.c., made up with water.

Reagent concentration : An increase in the rate of colour development was noticed with 2 c.c. of the reagent solution. Thus the maximum absorption of a solution containing 1 γ Co/c.c. was observed after 15 minutes with 2 c.c. of the reagent, while about half an hour was required for the same with 1 c.c. of the reagent. Further addition of the reagent solution was found to have no effect on the rate of colour development.

Sodium hydroxide concentration : The optical density of the complex solution was almost unaffected by a very dilute sodium hydroxide solution. But with a fairly strong solution (*N*/4) the absorption gradually increased with time, and the colour changed slowly from orange-yellow to yellowish brown. This is probably due to the conversion of the cobaltous compound into one of a higher valency state.

Beer's Law.—The system was found to obey Beer's law in presence of sodium acetate (cf. Curve II, Fig. 2). The optical density measurements were made after 30 minutes from the addition of the reagent.

Stability of the colour.—The optical density of solutions, prepared without sodium acetate, showed increasing values with time. In presence of sodium acetate, however, the maximum colour intensity was reached within half an hour after addition of the reagent. The optical density of such solutions was found to remain constant for 2-3 hours at the room temperature.

Sensitivity : 0.003 γ Co/cm^2 (S) and 0.0025 γ Co/cm^2 (p).

Effect of diverse ions (cf. under copper).—It is possible to eliminate the interferences caused by copper and nickel by means of potassium cyanide solution added after the development of maximum colour. Potassium cyanide discharges the colour

due to copper and nickel, without appreciably affecting that of cobalt. The optical density is to be measured after one hour from the addition of potassium cyanide. This ensures the complete discharge of the colour due to copper and nickel. In the presence of foreign ions a stronger solution of the reagent is to be used. It can be prepared by dissolving 0.25 g. of *NN'*-diphenylrubeanic acid in 50 c.c. of 2*N*-NaOH solution. 2 c.c. of this solution was used when both copper and nickel were present in the sample solution. 5 c.c. of potassium cyanide solution has been found to be sufficient for solutions containing 1 p.p.m. Co, in the presence of 30 p.p.m. Ni or 10 p.p.m. Cu.

Procedure.—To an almost neutral test solution 1 c.c. of 1% sodium acetate solution and 5 c.c. of pyridine were added. This was diluted to about 20 c.c. and treated with 2 c.c. of the reagent solution. The volume was then made up to 25 c.c. with water and the optical density measured at 410 mμ after 15-20 minutes. A reagent blank was always used for measurements. In presence of copper or nickel, precautions noted above should be taken.

Determination of Nickel

The following solutions were used: Standard nickel solution, 0.05 mg./c.c. All other solutions were the same as those used for the cobalt determination.

Absorption maximum: 510 mμ at which measurements were made (cf. Curve III, Fig 1).

An excess of pyridine or reagent solution had no effect on the colour intensity (cf. under cobalt).

NaOH *concentration*: Very dilute sodium hydroxide solution was without any appreciable effect on the optical density of the complex solution; but an excess of the alkali solution was found to diminish the intensity of the colour. Thus for 2 p.p.m. Co, 5 c.c. of *N*/2 sodium hydroxide diminished the intensity by about 20%.

Beer's Law.—The system obeyed Beer's law (cf. Curve III, Fig. 2). At higher concentrations of nickel (>4 p.p.m.), presence of sodium acetate was helpful for the rapid development of the maximum colour intensity.

Stability of the colour: About 15-20 minutes were required for the attainment of maximum colour intensity. This time lag was more noticeable at higher concentrations of Co (>4 p.p.m.). About 2% increase in absorption was observed after 20 hours at the room temperature.

Sensitivity: 0.0075 γ Ni/cm² (S) and 0.03 γ Ni/cm² (p).

Effect of diverse ions: (cf. under copper and cobalt).

Procedure.—Pyridine (5 c.c.) was added to the test solution, which was almost neutral and free from interfering ions. This was followed by 10 c.c. of water and then 3 c.c. of the reagent solution. The mixture was shaken well for about 2-3 minutes and the volume made up to 25 c.c. with distilled water. After half an hour the optical density of the pink-red solution was measured at 510 mμ against a reagent blank. A solution of sodium acetate (1 c.c. of 1%) can be added before adding the reagent solution for the rapid development of colour.

Determination of Palladium

The following solutions were used: Standard palladium solution (0.05 mg. Pd per c.c.) and the reagent solution as for cobalt.

Absorption maximum: At about 395 mμ at which measurements were made (cf. Curve IV, Fig. 1).

Pyridine concentration: 5 c.c. in a total volume of 25 c.c., made up with water.

Reagent concentration: 1 c.c. of the reagent for Pd up to 0.1 mg. in 25 c.c. final volume.

NaOH *concentration*: An excess of the alkali retards the colour development. Thus with 5 c.c. of $N/4$ sodium hydroxide solution the maximum colour intensity was developed only after half an hour.

Beer's Law.—The system was found to obey Beer's law (cf. Curve III, Fig. 2). For palladium concentration more than 4 p.p.m., 3 c.c. of the reagent were added instead of 1 c.c.

Stability of the colour.—The colour was produced instantaneously on adding the reagent solution, and was stable for more than 24 hours at the room temperature.

Sensitivity: 0.0075 γ Pd/cm^2 (S) and 0.025 γ Pd/cm^2 (p).

Procedure.—To the palladium solution, which was separated from the interfering ions, 5 c.c. of pyridine, 5 c.c. of water and 1-3 c.c. (depending upon the palladium concentration) of the reagent solution were added in the order given. The volume was finally made up to 25 c.c. with water and the optical density measured at 395 mμ against a reagent blank.

Detection of Ruthenium

Ruthenium solutions, when warmed with *NN'*-diphenylrubeanic acid, develop a greenish blue coloration. But the precipitation of the complex occurs within a short time. However, it was possible to detect small amounts of ruthenium in the following manner: To the sample solution 2 c.c. of a mixture (1 : 1) of ethyl alcohol (95%) and concentrated hydrochloric acid (11*N*), and 1 c.c. of 0.01% alcoholic solution of the reagent were added. The mixture was warmed on a water-bath for about 5 minutes. A greenish yellow or a light green colour developed when ruthenium was present. The test was carried out in comparison with a blank containing the same amount of the reagent solution. By this means 0.06 γ Ru could be identified at a concentration limit of $1 : 5 \times 10^7$.

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AN ANALYSIS OF THE NEUTRALISATION CURVES OF THE COLLOIDAL ACIDS. PART VI

By S. L. Gupta and M. Adhikari

It is shown that the conductometric neutralisation curves for the colloidal clay acids can be constructed theoretically which compare favourably with experimental, from a knowledge of the counter ions obtained by p_H and a_M determinations. It has been suggested that these colloidal electrolytes are of the uni-univalent type and some of the special characteristics attributed to the double layers surrounding the particles for the interpretation of the conductometric neutralisation curves are unnecessary.

In previous communications (Gupta, Parts I-V, this *Journal*, 1956, **33**, 587; 1957, **34**, 63, 691, 696, 743) it has been shown that the curves for p_H, a_M and specific conductivity, during the neutralisation of colloidal acids, against concentration of added base are related, and if the curves happen to be of the theoretical type, viz., Bradfield type (Part V, *loc. cit.*) then it is possible to predict the a_M curve (Part III, *loc. cit.*) or the specific conductivity curve (Part II, *loc.cit.*) from the p_H curve alone by evaluating a series of dissociation constants. For curves of the irregular type, as obtained by Marshall, which do not fit in with any of the equations for reasons discussed earlier (Part V *loc. cit.*), two curves, *i. e.*, p_H and a_M, are necessary to predict the third curve, *i.e.*, the specific conductivity curve. The present communication seeks to demonstrate this fact with already published informations on the neutralisation of some clay acids.

The necessary experimental data, presented here for the purpose of evaluation and comparison, have been obtained from the works of Marshall and Krinbill (*J. Phys. Chem.*, 1942, **46**, 1077). The data consist of values of p_H, a_{Na^+} and specific conductivity during the neutralisation of acid clay suspensions of each of the four clay minerals, Beidellite, Montmorillonite, Illite and Kaolinite, with increasing addition of the titrating alkali, *i.e.*, NaOH. In the same paper the authors have calculated the cationic contribution to the total conductance and have shown that there remains a gap between the two values ascribed to the anionic contribution, which becomes wider as the titration proceeds. The present calculations show that the gap can be effectively closed if the anionic contributions are added to those of the cations. For the computation of the specific conductivity, the equation employed is

$$\kappa = \frac{U_{Na^+}(a_{Na^+})_t + U_{H^+}(a_{H^+})_t + V_{OH^-}(a_{OH^-})_t + V_{R^-}(a_{Na^+} + a_{H^+} - a_{OH^-})_t}{1000}$$

where the symbols have their usual significances (note the misprint of this equation in Part IV, *loc. cit.*). In the above equation V_{R^-}, it will be remembered, represents the limiting conductance of the clay particles per equivalent of charge on the clay surface and the amount of charge in equivalents is given by $(a_{Na^+} + a_{H^+} - a_{OH^-})_t$. The following values have been assumed: $U_{Na^+} = 50.11$, $U_{H^+} = 349.82$, and $V_{OH^-} = 198.5$ mhos cm^2 equiv.$^{-1}$ respectively at 25°. The values of V_{R^-} necessary to give a good fit had to be obtained by trial for each of the four clay minerals. Thus, it has been found that the following values of V_{R^-} in mhos cm^2 equiv.$^{-1}$ fit the data satisfactorily: 35 for Beidellite, 40 for Montmorillonite, 55 for Illite and 60 for Kaolinite.

TABLE I

Putnam clay (Beidellite), fraction < 0.2μ. Anionic conductance = 35 mhos cm^2 equiv.$^{-1}$.

'b' NaOH (moles/litre).	p_H.	$(a_{Na^+})_t$.	$(a_{H^+})_t$.	$(a_{OH^-})_t$.	$(a_{Na^+}+a_{H^+}-a_{OH^-})_t$.	Sp. cond. (mhos). Calc.	Obs.	Thixotropic setting time.
				10% Suspension				
0.00×10^{-2}	3.80	$0.00\times10^{-3}N$	$1.585\times10^{-4}N$		$0.1585\times10^{-3}N$	0.61×10^{-4}	0.622×10^{-4}	
1.04	5.27	1.07	5.37×10^{-5}		1.075	0.93	1.25	
2.08	5.52	1.86	3.02×10^{-5}		1.86	1.59	1.92	
3.13	5.57	3.62	2.69×10^{-6}		3.62	3.08	3.26	0 sec.
6.8	7.00	11.9		Negligible.	11.9	10.12	...	0
7.3	8.09	14.3		$1.23\times10^{-6}N$	14.3	12.19	8.9	72
7.82	8.95	15.0		8.91×10^{-6}	15.0	12.77	10.3	
9.4	10.58	24.6		3.80×10^{-4}	24.2	21.50	18.8	
11.5	11.44	35.7		2.75×10^{-3}	32.95	34.90	39.9	
				7% Suspension.				
0.00×10^{-2}	3.83	$0.00\times10^{-3}N$	$1.47\times10^{-4}N$		$0.148\times10^{-3}N$	0.565×10^{-4}	0.656×10^{-4}	
0.361	4.77	...	1.70×10^{-5}		...	...	1.520	
0.721	5.44	0.87	3.63×10^{-6}		0.87	0.752	0.916	
1.44	5.70	1.42	2.00×10^{-6}		1.40	1.27	1.37	
2.16	5.75	2.32	1.78×10^{-6}		2.32	1.98	2.02	
2.88	5.75	3.32	1.78×10^{-6}		3.32	2.81	2.91	30 min.
3.61	6.03	4.22	9.33×10^{-7}		4.22	3.59	3.32	6
3.96	6.20	5.06			5.06	4.34		0
4.22	6.54	5.37			5.37	4.57	4.31	15
4.68	7.03	6.03		Negligible	6.03	5.10	4.73	
5.05	8.08	7.93		$1.20\times10^{-6}N$	7.93	6.75	6.12	
5.40	8.94	8.77		8.71×10^{-6}	8.76	7.46	6.44	
6.48	10.54	14.00		3.47×10^{-4}	13.66	12.48	12.20	
7.93	11.35	23.50		2.24×10^{-3}	21.66	24.00	27.00	

TABLE II

Bentonite (Montmorillonite), fraction $< 0.2\mu$. Anionic conductance = 40 mhos cm^2 equiv.$^{-1}$.

'b' NaOH (moles/litre)	p_H.	$(a_{Na^+})_t$.	$(a_{H^+})_t$.	$(a_{OH^-})_t$.	$(a_{Na^+}+a_{H^+}-a_{OH^-})_t$.	Sp. cond. (mhos) Calc.	Sp. cond. (mhos) Obs.	Thixotropy.
				2.8% Suspension.				
0.000×10^{-2}	2.87	$0.00 \times 10^{-3}N$	$1.35 \times 10^{-3}N$		$1.35 \times 10^{-3}N$	5.26×10^{-4}	4.15×10^{-4}	
0.142	3.23	...	5.89×10^{-4}		...	...	2.91	
0.425	4.09	1.75	8.13×10^{-5}		1.83	2.09	2.16	
0.994	5.08	2.56	8.32×10^{-6}		2.57	2.34	2.64	
1.56	5.33	4.17	4.67×10^{-6}		4.17	3.77	3.36	
1.99	5.66	5.45	2.19×10^{-6}		5.45	4.91	4.31	Present
2.27	5.88	5.47	1.32×10^{-6}		5.47	4.93	4.15	Maximum
2.41	6.02	5.63			5.63	5.07	4.31	Present
2.55	6.73	6.47		Negligible	6.47	5.88	4.73	
2.69	7.30	8.73			8.73	7.86	5.11	
2.84	8.24	10.80		$1.74 \times 10^{-6}N$	10.80	9.73	6.04	
3.12	9.51	12.20		3.24×10^{-5}	12.17	11.00	7.18	
3.41	10.07	14.80		1.18×10^{-4}	14.70	13.50	8.96	
3.97	11.10	19.00		1.26×10^{-3}	17.74	19.00	15.70	
				1.0% Suspension.				
0.000×10^{-2}	3.23	$0.00 \times 10^{-3}N$	$5.89 \times 10^{-4}N$		$0.589 \times 10^{-3}N$	2.29×10^{-4}	2.17×10^{-4}	
0.151	4.30	0.48	5.01×10^{-5}		0.53	0.63	1.08	
0.553	5.88	1.20	1.32×10^{-6}		1.20	1.10	1.23	
0.803	6.35	1.49	4.47×10^{-7}		1.49	1.34	1.43	
0.853	6.43	1.55			1.55	1.40	1.43	
0.904	6.75	1.70		Negligible	1.70	1.53	1.60	
0.954	7.08	1.95			1.95	1.76	1.85	
1.100	8.99	2.76		$9.77 \times 10^{-6}N$	2.75	2.49	2.48	
1.210	9.69	3.37		4.90×10^{-5}	3.32	3.11	3.12	
1.410	10.57	5.30		3.72×10^{-4}	4.93	5.37	5.52	

TABLE III

Illinois "grundite", (Illite), fraction $< 2\mu$. Anionic conductance = 55 mhos cm^2 equiv.$^{-1}$.

"b" NaOH (moles/litre).	p_H.	$(a_{Na^+})_f$.	$(a_{H^+})_f$.	$(a_{OH^-})_f$.	$(a_{Na^+}+a_{H^+}-a_{OH^-})_f$.	Sp. cond. (mhos). Calc.	Obs.
			10% Suspension.				
0.0×10^{-3}	3.49	$0.00\times10^{-3}N$	$3.236\times10^{-4}N$		$3.236\times10^{-4}N$	13.10×10^{-5}	7.68×10^{-5}
5.2	5.40	0.557	3.98×10^{-6}		5.61	6.01	5.74
8.3	5.74	0.663	1.82×10^{-6}		6.65	7.04	6.65
12.5	6.00	0.928	1.00×10^{-6}		9.29	9.74	8.33
16.7	6.22	1.21			12.1	12.7	10.6
20.8	6.54	1.49		Negligible	14.9	15.6	12.3
25.0	7.43	2.29			22.9	24.0	18.5
29.9	8.77	3.58		$5.89\times10^{-6}N$	35.7	37.6	29.6
33.3	9.85	5.45		7.08×10^{-5}	53.8	58.3	47.7
37.5	10.70	9.56		5.01×10^{-4}	90.6	107.4	84.5
			5% Suspension.				
0.0×10^{-3}	3.71	$0.00\times10^{-3}N$	$1.98\times10^{-4}N$		$1.95\times10^{-4}N$	7.89×10^{-5}	5.98×10^{-5}
2.55	5.58	0.238	2.63×10^{-6}		2.40	2.60	3.22
4.08	6.09	0.284	1.00×10^{-6}		2.84	2.98	3.65
6.12	6.27	0.361	5.37×10^{-7}		3.61	3.79	4.37
8.15	6.49	0.473			4.73	4.97	5.48
10.20	6.79	0.592		Negligible	5.92	6.22	6.50
12.20	7.48	0.899			8.99	9.45	9.73
14.30	8.62	1.430		$4.17\times10^{-6}N$	14.30	15.10	15.80
16.30	9.52	2.280		3.31×10^{-5}	22.50	27.30	26.20
18.40	10.26	3.690		1.82×10^{-4}	35.10	41.40	45.20

6—1970 P—10

TABLE IV

Kaolinite, fraction $< 2\mu$. Anionic conductance = 60 mhos cm^2 equiv. $^{-1}$

'b' NaOH (moles/litre)-	p_H.	$(a_{Na^+})_f$.	$(a_{H^+})_f$.	$(a_{OH^-})_f$.	$(a_{Na^+} + a_{H^+} - a_{OH^-})_f$.	Sp cond. (mhos). Calc.	Obs.
			10% Suspension-				
0.00×10^{-3}	4.62	$0.00 \times 10^{-4}N$	$2.40 \times 10^{-5}N$		$0.24 \times 10^{-4}N$	0.170×10^{-4}	0.113×10^{-4}
0.52	6.03	2.20	9.33×10^{-7}		2.20	0.228	0.269
1.04	6.35	2.88	4.47×10^{-7}		2.88	0.319	0.370
2.08	6.67	4.98			4.98	0.549	0.625
3.12	7.91	10.50			10.50	1.160	1.250
4.16	9.75	18.10		$5.62 \times 10^{-5}N$	17.54	2.070	2.020
5.20	10.34	26.30		2.19×10^{-4}	24.11	3.200	3.200
6.24	10.70	34.70		5.01×10^{-4}	29.69	4.500	4.790
7.28	10.95	43.60		8.91×10^{-4}	34.69	6.030	6.590

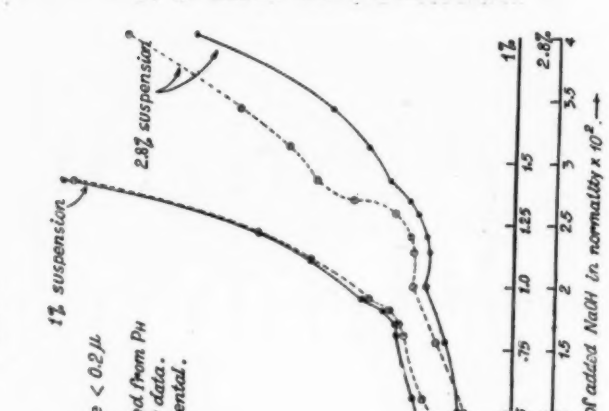

Bentonite < 0.2 μ
---Calculated from Pw and a Na+ data.
— Experimental.
1% suspension
2.8% suspension
Sp. Cond. x 10⁴
Conc. of added NaOH in normality x 10²

FIG. 2

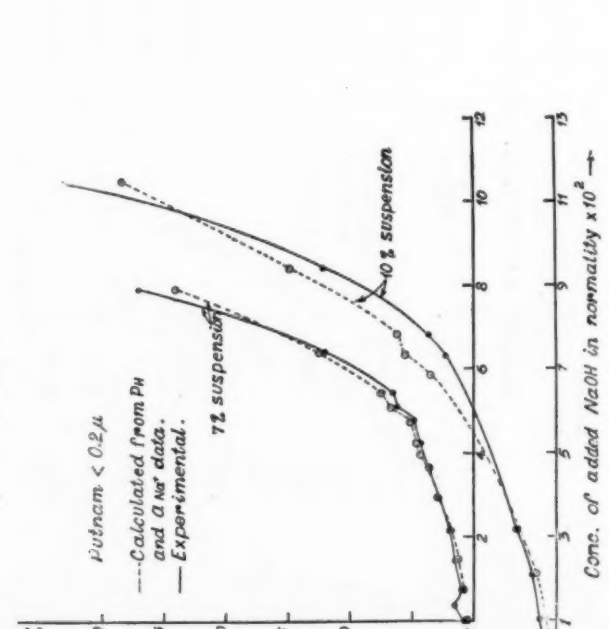

Putnam < 0.2 μ
---Calculated from Pw and a Na+ data.
— Experimental.
7% suspension
10% suspension
Sp. Cond. x 10⁴
Conc. of added NaOH in normality x 10²

FIG. 1

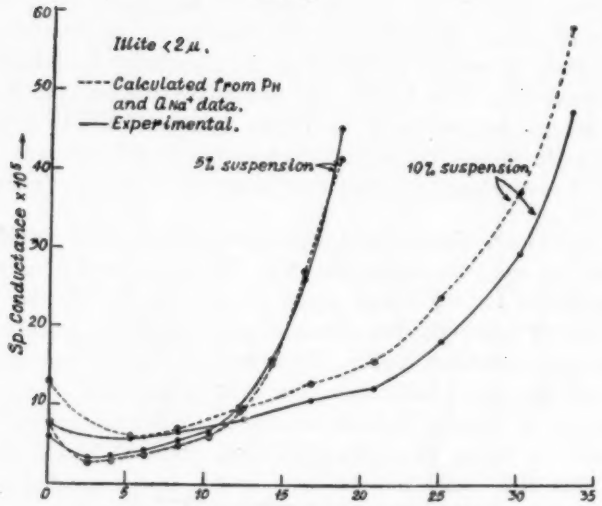
In the previous publications of this series, for the calculation of the specific conductivity of a clay sample (Part II, *loc. cit.*), and for the AgI sol (Part IV, *loc. cit.*) we used such values of anionic conductance for the charge on colloid surface. The present experimental fits, it is hoped, will strengthen such belief in the reality of the quantity. The results are presented in Tables I, II, III and IV and the calculated and observed values of the specific conductivities on 7th and 8th columns of the tables. For convenience of comparison the values are also shown graphically in Figs. 1 to 4.

It will be seen from the results that the calculated values of specific conductivity are more or less in complete agreement with the experimental ones in the case of the dilute suspensions for the whole range of titration for all the clay minerals, while in the case of relatively concentrated suspensions, the calculated specific conductivity values are somewhat higher. This may be due to our assumption of the limiting value of the ionic conductance for each of the ionic species, while, in fact, the values have to be reduced for concentrated suspensions according to the interionic attraction theory. A better fit might have been obtained by introducing the Onsager correction, but this could not be done as the said correction is on the basis of stoichiometric concentrations for strong electrolytes and not for electrochemically determined activities. The above consideration holds good particularly for Bentonite and Illite and it also holds good for Beidellite except for the last point. The calculated and experimental curves cross as the final calculated value is lower than the experimental for the curves of the last named clay mineral.

In the case of 1% Bentonite sample (Fig. 2), the second point is unusually low, causing some deviation in the initial stage between the calculated and the experimental curves. It will be seen from the data that for all other samples, the charge on the clay surface, given by figures in the 6th column of the tables, increases continuously from the beginning of the neutralisation as the neutralisation proceeds. This is demanded by the theory of weak acid neutralisation of clay suspensions (Part II, *loc. cit.*). In this particular case of 1% Bentonite, however, there is a diminution of particle charge at the second point. It seems that the recorded p_H value for this point is somewhat high. A slightly lower p_H value will bring this point in line with the experimental curve for specific conductivity. This is likely because this point falls on the initial rising part of the p_H curve where the clay sample may be considered to be highly unbuffered. A slight discrepancy of initial p_H reading seems also to exist in the case of Illite samples.

It is interesting to note, as pointed out by Marshall *et al.* (*loc. cit.*), that the region of thixotropy in 10% and 7% Beidellite and the 2.8% Bentonite is not characterised by any change in the conditions of conductance, as shown in these experiments. This confirms for the case of clays what has long been established for soaps by McBain, namely, "that the mechanism of conductance is not essentially different in gels from what it is in sols". This observation is important as it points to the difficulty of correlating viscosity measurements with neutralisation and also to the fact that the counter ions are obstructed in no way by thixotropic gelation.

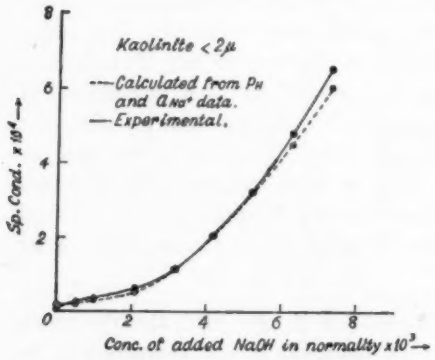
FIG. 3



It is apparent from the above analysis that the anionic conductance per equivalent of charge is highest in the case of Kaolinite and least in the case of Beidellite, the order being Kaolinite > Illite > Montmorillonite > Beidellite. The anionic conductances of Kaolinite and Illite clays are even greater than Na^+ ions.

Several irresistible conclusions present themselves from the above agreement as well as from our previous analyses of the neutralisation curves of other sols (Parts I-V, *loc. cit.*). These colloidal electrolytes are fundamentally of uni-univalent type, as pointed out by the McBain from a study of their soap solutions (cf. McBain, "Colloid Science", 1950, D. C. Heath & Co., p. 255; Gupta, *Science & Culture*, 1957-58, **23**, 103, 493), and it is possible to deal with these from classical standpoint without having to take recourse to some of the double layer characteristics. For example, the double layer theory holds that there is a gradation of binding strength between the cations of the double layer and the colloid surface which falls off with increasing distance from the wall. The cations nearer to the wall are more firmly bound and in the limit form a layer of adsorbed ions. Secondly, it assumes that because of this unequal binding strength, the conductance of the small ions is greater in the periphery and outside of the double layer than near to the surface (cf. Kruyt, "Colloid Science", Part I, 1950, Elsevier Publishing Co., p. 179). Thirdly, the demarcation line separa-

FIG. 4



ting the double layer from the intermicellar liquid is not clearly set, for example, one cannot say which part of the small ions belongs to the double layer and which part to the intermicellar solution (cf. Kruyt, *loc. cit.*, pp. 238-240). The present study shows that such assumptions are unnecessary. The adsorbed cations given by $a(_{Na^+})_a$ and $(a_{H^+})_a$ (Part I, *loc. cit.*), which are situated at an inner surface (Gupta, *Sceince & Culture*, 1957, **22**, 512 ; 1958, **23**, 366) do not contribute to the conductivity at all, while the free ions given by $(a_{Na^+})_f$, $(a_{H^+})_f$, $(a_{OH^-})_f$ and $(a_{R^-})_f$ contribute fully to the total conductivity just as in a solution of any uni-univalent electrolyte. The deviation for concentrated suspensions is due to causes dealt with by interionic attraction theory, and the Onsager correction becoming significant. Evidently, the reason for our assumption is, as has been repeatedly pointed out by McBain (*loc. cit.*), that the charges on the surface of the colloidal particles are so far apart that they have the properties of a uni-univalent electrolyte as if present in true solution. The prerequisite of assuming gradation of binding strength is to consider that the whole charge on a particle is concentrated at a central point within the particle, ignoring the large surface on which they are distributed, which picture is likely to be far from the real state of affairs.

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SUBSTITUTED BUTYRO LACTONES. PART III. SYNTHESIS OF γ-(4-ALKOXY-3-CHLOROPHENYL)-BUTYRO LACTONES

By Miss S. L. Dalal, J. J. Trivedi and N. Z. Patel*

β-(4-Alkoxy-3-chlorobenzoyl)-propionic acids, obtained by succinoylation of 2-chlorophenyl alkyl ethers, have been reduced to furnish γ-(4-alkoxy-3-chlorophenyl)- butyro lactones.

Importance of lactone ring and the alkoxy group (Genge and Trivedi, this *Journal*, 1957, **34**, 801, 804) as also of chlorophenyl group (Genge and Kshatriya, *ibid.*, 1958, **35**, 521, 525) has been discussed earlier. γ-(4-Alkoxy-3-chlorophenyl)-butyro lactones have been prepared and described in the present communication.

β-(4-Alkoxy-3-chlorobenzoyl)-propionic acids, required for preparation of the above lactones, were obtained by succinoylation of 2-chlorophenyl alkyl ethers. Nuguyen-Hoan and Buu Hoï (*Compt. rend.*, 1947, **224**, 1228) succinoylated (no details) 2-chloroanisole and 2-chlorophenetole to yield β-(4-methoxy-3-chlorobenzoyl)- and β-(4-ethoxy-3-chlorobenzoyl)-propionic acids respectively.

Ethyl esters of β-(4-alkoxy-3-chlorobenzoyl)-propionic acids were reduced by aluminium *iso*propoxide, and the resulting hydroxy-acids on lactonisation afforded γ-(4-alkoxy-3-chlorophenyl)-butyro lactones.

Experimental

2-Chlorophenyl alkyl ethers were prepared by the action of an appropriate alkyl bromide on 2-chlorophenol in presence of sodium ethoxide.

2-Chlorophenyl-n-hexyl ether does not seem to have been described before. It is a colorless liquid, b.p. 261°/760 mm, n_D^{40} 1.537. (Found: Cl, 16.6. $C_{12}H_{17}OCl$ requires Cl, 16.7%).

General Procedure for Succinoylation of 2-Chlorophenyl Alkyl Ethers.—This was carried out as described by Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1936, **58**, 2314) with the following modifications.

In the succinoylation of 2-chloroanisole and 2-chlorophenetole, nitrobenzene was used as a solvent. The reaction mixture was kept at 0° for 4 hours. In case of higher phenyl alkyl ethers, a mixed solvent was used. The reaction mixture was kept at 0° for 24 hours.

Ethyl β-(4-alkoxy-3-chlorobenzoyl)-propionates were reduced by aluminium *iso*-propoxide, as described by Genge and Trivedi (*loc. cit.*) to yield γ-(4-alkoxy-3-chlorophenyl)-butyro lactones. Compounds prepared are shown in Tables I and II.

* In part.

TABLE I

β-(4-n-Alkoxy-3-chlorobenzoyl)-propionic acids and derivatives.

No.	Compounds.	Cryst. shape.	M.P. or B p	Formula.	% Chlorine *. Found.	Calc.
1.	Oxime of β-4-methoxy-P †	Plates from benzene or dil. alcohol	120°	$C_{11}H_{12}O_4NCl$	13.53	13.78
2.	Semicarbazone of ,,	Needles from dil. EtOH	236°	$C_{12}H_{14}O_4N_3Cl$	11 98 (296.5)	11.85 (299.5)
3.	Ethyl ester of ,,	Do	90°	$C_{13}H_{15}O_4Cl$	12.80	13.12
4.	Methyl ester of ,,	Do	117°	$C_{12}H_{13}O_4Cl$	13.69	13.84
5.	Oxime of β- 4-ethoxy-P	Plates from benzene or dil. alcohol	130°	$C_{12}H_{14}O_4NCl$	13.21	13.06
6.	Semicarbazone of β-4-ethoxy-P	Needles from dil. EtOH	160°	$C_{13}H_{16}O_4N_3Cl$	11.20 (312.1)	11.32 (313.5)
7.	Ethyl ester of β-4-ethoxy-P	Do	70°	$C_{14}H_{17}O_4Cl$	12.10	12.47
8.	Methyl ester of ,,	Do	100°	$C_{13}H_{15}O_4Cl$	13.23	13.12
9.	β-4-n-Propoxy-P	Needles from alcohol or hot water	180°	$C_{13}H_{15}O_4Cl$	13.00 (272.6)	13.12 (270.5)
10.	Oxime of (9)	Plates from benzene	111°	$C_{13}H_{16}O_4NCl$	12.63	12.44
11	Ethyl ester of (9)	Needles from dil. EtOH	66°	$C_{15}H_{19}O_4Cl$	11.82	11.90
12.	Methyl ester of (9)	Do	80°	$C_{14}H_{17}O_4Cl$	12.39	12.48
13.	β-4-n-Butoxy-P	Do	150°	$C_{14}H_{17}O_4Cl$	12.60 (282 6)	12.48 (284 5)
14.	Oxime of (13)	Plates from benzene or dil. alcohol	118°	$C_{14}H_{18}O_4NCl$	11.68	11.85
15.	Ethyl ester of (13)	...	190-95°/4mm	$C_{16}H_{21}O_4Cl$	11.54	11.36
16.	Methyl ester of (13)	Needles from dil. alcohol	75°	$C_{15}H_{19}O_4Cl$	11.79	11.90
17.	β-4-n-Amyloxy-P	Do from dil. EtOH or hot water	102°	$C_{15}H_{19}O_4Cl$	11.73 (296.0)	11 90 (298.5)
18.	Oxime of (17)	Plates from benzene	120°	$C_{15}H_{20}O_4NCl$	11.48	11.32
19.	Ethyl ester of (17)	...	235-40°/10mm	$C_{17}H_{23}O_4Cl$	10.33	10.87
20.	β-4-n-Hexyloxy-P	Needles from dil. alcohol or hot water	80°	$C_{16}H_{21}O_4Cl$	11.50 (311.7)	11.36 (312.5)
21.	Ethyl ester of (20)	...	245-50°/10mm	$C_{18}H_{25}O_4Cl$	10.31	10.42

* Equivalent weights are shown in parentheses.

† P denotes -3-chlorobenzoyl)-propionic acid.

TABLE II

γ-(4-n-Alkoxy 3-chorophenyl)-butyro lactones and derivatives.

No.	Name of compound.	Cryst. shape.	M.P. or B.P.	Mol. formula.	% Chlorine*. Found.	Calc.
1.	γ-(4-Methoxy)-L	Prismatic plates from alcohol	74°	$C_{11}H_{11}O_3Cl$	15.40 (224.5)	15.67 (226.5)
2.	S-salt of γ-4-methoxy-HB	Plates from water	128°	$C_{19}H_{23}O_4N_2ClS$	8.80	8.67
3.	γ-(4-Ethoxy)-L	Prismatic plates from alcohol	82°	$C_{12}H_{13}O_3Cl$	14.51 (239 2)	14.76 (240.5)
4.	S-salt of γ-(4-ethoxy)-HB	Plates from water	140-41°	$C_{20}H_{25}O_4N_2ClS$	8.41	8.38
5.	γ-(4-*n*-Propoxy)-L		195-200°/3mm	$C_{13}H_{15}O_3Cl$	13.82 (256.1)	13.95 (254·5)
6.	S-salt of γ-(4-*n*-propoxy)-HB	Plates from water or alcohol	132°	$C_{21}H_{27}O_4N_2ClS$	8.03	8.11
7.	γ-(4-*n*-Butoxy)-L		180-85°/3mm	$C_{14}H_{17}O_3Cl$	12.92 (265 3)	13.22 (268.5)
8.	S salt of γ-(4-*n*-butoxy)-HB	Plates from water or alcohol	128°	$C_{22}H_{29}O_4N_2ClS$	7.81	7.86
9.	γ-(4-*n*-Butoxy)-HB	Plates from benzene	80°	$C_{14}H_{19}O_4Cl$	12.25 (284.3)	12.39 (286.5)
10.	γ-(4-*n*-Amyloxy)-L		200-205°/6mm	$C_{15}H_{19}O_3Cl$	12.81 (280 4)	12.57 (282.5)
11.	S-salt of γ-(4-*n*-amyloxy)-HB	Plates from water	108°	$C_{23}H_{31}O_4N_2ClS$	7.53	7.62
12.	γ-(4-*n*-Hexyloxy)-L		208-12°/6mm	$C_{16}H_{21}O_3Cl$	11.75 (295.5)	11.98 (296.5)
13.	S-salt of γ-(4-*n*-hexyloxy)-HB	Plates from water	85°	$C_{24}H_{33}O_4N_2ClS$	7.23	7.40

S stands for *S*-benzyl *iso*thiuronium.
HB (-3-chlorophenyl)-hydroxybutyric acid.
L (,, ,,)-butyro lactone.
* Equivalent weights are shown in parentheses.

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SUBSTITUTED BUTYRO LACTONES. PART IV. SYNTHESIS OF γ-(2-ALKOXY-5-CHLOROPHENYL)-BUTYRO LACTONES

By Miss S. L. Dalal, J. J. Trivedi and N. Z. Patel*

Ethyl β-(2-alkoxy-5-chlorobenzoyl)-propionates have been reduced by aluminium *iso*propoxide to γ-(2-alkoxy-5-chlorophenyl)-butyro lactones.

In continuation of the work described in Part III of the series (this *issue*, p. 742) γ-(2-alkoxy-5-chlorophenyl)-butyro lactones have been prepared and described in this communication. Attempt was made to succinoylate 4-chlorophenyl alkyl ethers to obtain the required β-(2-alkoxy-5-chlorobenzoyl)-propionic acids. Succinoylation of 4-chloroanisole afforded β-(2-methoxy-5-chlorobenzoyl)-propionic acid in 90% yield. Constitution of this acid rests on the fact that on oxidation it gives rise to a product identical (m.p. and mixed m.p. 81-82°) with methyl ether of 5-chlorosalicylic acid (Peratoner and Condorelli, *Gazzetta*, 1898, **28**, 211).

In the case of higher 4-chlorophenyl alkyl ethers, the keto-acids were partially dealkylated. Therefore β-(2-alkoxy-5-chlorobenzoyl)-propionic acids were prepared by alkylating ethyl β-(2-hydroxy-5-chlorobenzoyl)-propionate (Trivedi and Nargund, *J. Univ. Bombay*, 1942, **2**, Part III, 127).

β-(2-Hydroxy-5-chlorobenzoyl)-propionic acid was prepared by the following two methods: (*a*) β-(2-Methoxy-5-chlorobenzoyl)-propionic acid was demethylated by hydrobromic acid in acetic acid solution and (b) 4-chlorophenol was succinoylated in presence of anhydrous aluminium chloride in tetrachloroethane.

Ethyl β-(2-alkoxy-5-chlorobenzoyl)-propionates were reduced by aluminium *iso*propoxide, as described by Genge and Trivedi (this *Journal*, 1957, **34**, 801) to obtain γ-(2-alkoxy-5-chlorophenyl)-butyro lactones.

Experimental

4-Chlorophenyl alkyl ethers were prepared from 4-chlorophenol and alkyl bromide in presence of sodium ethoxide. 4-Chlorophenyl-*n* propyl and -*n*-butyl ethers do not seem to have been described previously.

* In part

TABLE I

β-(2-Alkoxy-5-chlorobenzoyl)-propionic acids and derivatives.

S. No.	Compounds.	Cryst. shape.	M.P. or B.P.	Formula.	% Chlorine.* Found.	Calc.
1.	β-(2-Methoxy)-P†	Needles from hot water	120°	$C_{11}H_{11}O_4Cl$	14.20 (244.2)	14.64 (242.5)
2.	Oxime of (1)	Plates from dil. alcohol	168°	$C_{11}H_{12}O_4NCl$	13.67	13.78
3.	Semicarbazone of (1)	Needles from dil. alcohol	180°	$C_{12}H_{14}O_4N_3Cl$	11.57	11.85
4.	Ethyl ester of (1)		190-95°/6mm	$C_{13}H_{15}O_4Cl$	13.31	13.12
5.	β-(2-Ethoxy)-P	Needles from hot water	157°	$C_{12}H_{13}O_4Cl$	14.05 (257.9)	13.84 (256.5)
6.	Oxime of (5)	Plates from benzene	100°	$C_{12}H_{14}O_4NCl$	13.18	13.07
7.	Ethyl ester of (5)		180-85°/3mm	$C_{14}H_{17}O_4Cl$	12.70	12.48
8.	β-(2-*n*-Propoxy)-P	Needles from dil. alcohol	150°	$C_{13}H_{15}O_4Cl$	12.98 (268.1)	13.12 (270.6)
9.	Ethyl ester of (8)		55° 200-205°/10mm	$C_{15}H_{19}O_4Cl$	11.85	11.90
10.	β-(2-*n*-Butoxy)-P	Needles from dil. alcohol or hot water	110°	$C_{14}H_{17}O_4Cl$	12.70 (282.4)	12.48 (284.5)
11.	Oxime of (10)	Plates from benzene	145°	$C_{14}H_{18}O_4NCl$	11.64	11.85
12.	Ethyl ester of (10)		235-40°/9mm	$C_{16}H_{21}O_4Cl$	11.58	11.36
13.	β-(2-*n*-Amyloxy)-P	Needles from alcohol or hot water	101-102°	$C_{15}H_{19}O_4Cl$	12.02 (259.9)	11.90 (298.5)
14.	Oxime of (13)	Plates from dil. alcohol or benzene	112°	$C_{15}H_{20}O_4NCl$	11.47	11.32
15.	Ethyl ester of (13)		235-40°/4mm	$C_{17}H_{21}O_4Cl$	10.68	10.87
16.	β-(2-*n*-Hexyloxy)-P	Needles from dil. alcohol or hot water	106°	$C_{16}H_{21}O_4Cl$	11.23 (310.2)	11.36 (312.5)
17.	Ethyl ester of (16)		200-205°/6mm	$C_{18}H_{25}O_4Cl$	10.29	10.42
18.	β-(2-Hydroxy)-P	Do	178°	$C_{10}H_9O_4Cl$	15.80	15.53
19.	Semicarbazone of (18)	Needles from dil. alcohol	248°	$C_{11}H_{12}O_4N_3Cl$	12.32 (286.3)	12.44 (285.5)
20.	Ethyl ester of (18)	Do	80°	$C_{12}H_{13}O_4Cl$	13.62	13.84
21.	Methyl ester of (18)	Do	50°	$C_{11}H_{11}O_4Cl$	14.59	14.64

†P stands for -5-chlorobenzoyl)-propionic acid.

*Figures within parantheses represent equiv. wts.

4-Chlorophenyl-n-propyl ether is a colorless liquid, b.p. 224-25°/760 mm, d_4^{40} 1.092, n_D^{40} 1.570. (Found : Cl, 20.70. $C_9H_{11}OCl$ requires Cl, 20.80%).

4-Chlorophenyl-n-butyl ether is a colorless liquid, b.p. 240°/760 mm, d_4^{40} 1.098 ; n_D^{40} 1.508. (Found : Cl, 19.13. $C_{10}H_{13}OCl$ requires Cl, 19.24%).

β-(2-Methoxy-5-chlorobenzoyl)-propionic acid was prepared in 90% yield by succinoylating 4-chlorophenyl methyl ether as described in Part III (*loc. cit.*).

β-(2-Hydroxy-5-chlorobenzoyl)-propionic Acid.—(*a*). A mixture of β-(2-methoxy-5-chlorobenzoyl)-propionic acid (50 g.), acetic acid (100 c.c.) and hydrobromic acid (250 c.c., 48%) was refluxed for 2 hours on a sand-bath. The (2-hydroxy-5-chlorobenzoyl)-propionic acid, separating on cooling, was filtered and washed with water (yield 70%). It crystallised in needles from hot water, m.p. 178°.

(*b*). To a cooled mixture of 4-chlorophenol (25.6 g., 0.2 *M*), succinic anhydride (20 g., 0.2 *M*) and tetrachloroethane (200 c.c.) was added powdered anhydrous aluminium chloride (54 g., 0.4 *M*) in three lots, with stirring. It was then heated on an oil-bath at 120° for 2 hours. It was decomposed with ice and HCl and the keto-acid was recovered as usual after removing tetrachloroethane by steam distillation; yield 40%. Acid obtained by method (*b*) is identical (mixed m.p.) with that obtained by method (a).

Ethyl β-(2-hydroxy-5-chlorobenzoyl)-propionate was obtained from this acid by the usual procedure.

TABLE II

γ-(2-Alkoxy-5-chlorophenyl)-butyro lactones and derivatives.

S. No.	Compounds.	Cryst. shape.	M.P. or B.P.	Formula.	% Chlorine. Found.	Calc.
1.	γ-(2-Methoxy)-L		185-90°/3mm	$C_{11}H_{11}O_3Cl$	15.35 (222.3)	15.67 (226.5)
2.	S-salt of γ-(2-methoxy)-HB	Plates from hot water	102°	$C_{19}H_{21}O_4N_2ClS$	8.80	8.67
3.	γ-(2-Methoxy)-HB	Plates from benzene	100°	$C_{11}H_{13}O_4Cl$	14.80 (245.9)	14.52 (244.5)
4.	γ-(2-Ethoxy)-L		240-45°/3 mm	$C_{12}H_{13}O_3Cl$	14.95 (242.0)	14.76 (240.5)
5.	γ-(2-Ethoxy)-HB	Plates from benzene	103°	$C_{12}H_{15}O_4Cl$	11 07 (259.8)	10.91 (258.8)
6.	γ-(2-*n*-Propoxy)-L		215-20°/7 mm	$C_{13}H_{15}O_3Cl$	13.82 (251.6)	13.95 (254.5)
7.	γ-(2-*n*-Propoxy)-HB	Plates from benzene	105°	$C_{13}H_{17}O_4Cl$	13.18	13.02
8.	γ-(2-*n*-Butoxy)-L		220-25°/4 mm	$C_{14}H_{17}O_3Cl$	12.98 (265.3)	13.22 (268.5)
9.	S-salt of γ-2-*n*-butoxy-HB	Plates from hot water	85°	$C_{22}H_{29}O_4N_2ClS$	7.92	7.86
10.	γ-(2-*n*-Amyloxy)-L		215-18°/4 mm	$C_{15}H_{19}O_3Cl$	12.80 (284.1)	12.57 (282.5)
11.	S-salt of γ-(2-*n*-amyloxy)-HB	Do	85°	$C_{23}H_{31}O_4N_2ClS$	7.54	7.62
12.	γ-(2-*n*-Hexyloxy)-L		224-30°/3 mm	$C_{16}H_{21}O_3Cl$	11 70 (293.9)	11.98 (296.5)
13.	S salt of γ-(2-*n*-hexyloxy-HB)	Do	80°	$C_{24}H_{33}O_4N_2ClS$	7.33	7.40

HB stands for -5-chlorophenyl-γ-hydroxy butyric acid.
L „ „ „ „ butyro lactone.
S „ „ *S*-benzyl *iso*thiuronium.

β-(2-Alkoxy-5-chlorobenzoyl)-propionic acids were prepared by alkylation of ethyl β-(2-hydroxy-5-chlorobenzoyl)-propionate and subsequent hydrolysis (Trivedi and Nargund, *loc. cit.*).

Ethyl β-(2-alkoxy-5-chlorobenzoyl) propionates were reduced by aluminium *iso*-propoxide, and the lactones were isolated as described by Genge and Trivedi (*loc. cit.*), yield 40-50%.

The compounds prepared are shown in Tables I and II.

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SEARCH FOR NEW INSECTICIDES. PART II

By Shiva Shankar Tiwari and Akhileshwar Singh

o-Hydroxyketones of five esters of 4-chloro-3 : 5-dimethylphenol have been prepared by the Fries migration and have been converted into their allyl ethers with a view to studying their insecticidal activity.

In continuation of our previous work (Tiwari *et al.*, this *Journal*, 1954, **31**, 766; 1957, **34**, 830), we have now prepared allyl derivatives of hydroxyketones obtained by the rearrangement of esters of 4-chloro-3 : 5- dimethylphenol.

In keeping with the observation of Läuger *et al.* (*Helv. Chim. Acta*, 1944, **27**, 918) that allyloxy or aryl ethers are good contact insecticides because of their having a combination of toxic and lipoid-soluble grouping in their molecule, we have prepared five compounds containing allyl groups as toxophores and the ether linkage having lipophillic properties (cf. Chen and Sumerford, *J. Amer. Chem. Soc.*, 1951, **73**, 4694). These compounds also contain chlorine atom in the nucleus which might increase the toxicity, and ketonic group which might increase the lipoid solubility.

Five esters of *p*-chloro-*m*-xylenol, viz., propionate, butyrate, valerate, caproate and heptylate, were obtained either by Chattaway's method (*J. Chem. Soc.*, 1931, 2495) or by Spasov's method (*Chem. Abst.*, 1940, 2343).

The Fries rearrangement in the present investigation was studied at 110° with or without solvent. In all these cases studied, *o*-hydroxyketones were obtained, as confirmed by Pyman's test (*J. Chem. Soc.*, 1930, 280).

Experimental

The five esters of *p*-chloro *m*-xylenol, prepared according to methods described previously (cf. Sen and Tiwari, this *Journal*, 1952, **29**, 358), are described in Table I.

Table I

	p-Chloro-*m*-xylenol esters.	%Yield.	B.P.	Formula.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.
1.	Propionate	78.0	123°/3 mm	$C_{11}H_{13}O_2Cl$	62.07	62.13	6.11	6.12
2.	Butyrate	62.0	135°/3	$C_{12}H_{15}O_2Cl$	63.41	63.57	6.61	6.62
3.	Valerate	85.0	269°/7	$C_{13}H_{17}O_2Cl$	64.80	64.86	7.06	7.07
4.	Caproate	89.0	145°/1	$C_{14}H_{19}O_2Cl$	65.70	66.10	7.44	7.47
5.	Heptylate	79.0	174°/3	$C_{15}H_{21}{}_2Cl$	67.00	67.04	7.67	7.82

* Prepared by Chattaway's method.

Fries Rearrangement of the Esters.—The ester (1.0 *M*) was rearranged by keeping it with anhydrous aluminium chloride (1.5 *M*) in anhydrous CS_2 (6 0 *M*), for 2 hours at 80°. After distilling off the solvent the temperature of the mixture was raised to 110° and maintained at 110° for 2 hours. The hydroxyketones were isolated, purified and characterised in the usual way (Table II).

TABLE II

	p-Chloro-m-xylenol esters.	Ketone formed.	Cryst. from.	Cryst. shape.	Yield.	M.P.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.
1.	Propionate	R-ethyl-K	EtOH	Yellowish white	76%	106°	62.04	62 13	6.11	6.12
2.	Butyrate	R-*n*-propyl*-K	Do	Do	96	76°	63.31	63. 7	6 61	6.62
3.	Valerate	R-*n*-butyl-K	Do	White	73	63°	64.76	64 86	7.03	7.07
4.	Caproate	R-*n*-amyl-K**	EtOH or AcOH	Do	86	80°	65.87	65.10	7 40	7.47
5.	Heptylate	R-*n*-hexyl-K	Do	Do	69	79°	66.59	67 04	7.81	7.82

	Semicarbazone. Mol. formula	M P.	%Nitrogen. Found.	Calc.
1.	$C_{12}H_{16}O_2N_3Cl$	212°	15.95	15 95
	$C_{13}H_{18}O_2N_3Cl$	225°	15 72	15.81
3.	$C_{14}H_{20}O_2N_3Cl$	200°	13.92	14.12
4.	$C_{15}H_{22}O_2N_3Cl$	152°	13.47	13.49
5.	$C_{16}H_{24}O_2N_3Cl$	154°	12.55	12.90

* Using CS_2 as solvent.
** Without solvent yield is very poor.

N.B. Molecular formula of the ketone is the same as that of the ester.
-K denotes ketone; R- denotes 2-hydroxy-5-chloro-4: 6-dimethylphenyl-.

The *o*-hydroxyketones, obtained by the Fries rearrangement of these esters, were characterised through their semicarbazones (Table II), as 2 : 4-dinitrophenylhydrazones could not be isolated.

These *o*-hydroxyketones were further converted into allyl ethers (Table III), but these ethers could not be converted into their 2 : 4-dinitrophenylhydrazones or semicarbazones.

TABLE III

	Hydroxy-ketones.	Ether formed.	Yield.	B.P.	Formula.	%Carbon. Found.	%Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1.	R-ethyl-K	R'-ethyl-K	81%	54° (m p.)	$C_{14}H_{17}O_2Cl$	66.44	66.53	6.72	6 73
2.	R-*n*-propyl-K	R'-*n*-propyl-K	95	158°/1 mm	$C_{15}H_{19}O_2Cl$	67.50	67.54	7.08	7.13
3.	R-*n*-butyl-K	R'-*n*-butyl-K	98	160°/3	$C_{16}H_{21}O_2Cl$	68.36	68.43	7 45	7.49
4.	R-*n*-amyl-K	R'-*n*-amyl-K	69	190°/2	$C_{17}H_{23}O_2Cl$	69.20	69.28	7.71	7.81
5.	R-*n*-hexyl-K	R'-*n*-hexyl-K	87	187°/2	$C_{18}H_{25}O_2Cl$	69.88	70.01	7.90	8.10

N.B. Semicarbazone and 2 : 4-dinitrophenylhydrazone not separated.
K-denotes ketone; R' denotes 2-allyloxy-5-chloro-4: 6-dimethylphenyl-.
R-denotes 2-hydroxy-5-chloro-4: 6-dimethylphenyl-.

Allyl-aryl Ethers.—A mixture of allyl bromide (0.11 *M*), freshly fused potassium carbonate (0.11 *M*) and anhydrous acetone (40 c.c.) was refluxed on a water-bath for 6 hours. After cooling, ice was added and acetone was distilled off. The oily layer was taken in ether. The ethereal layer was washed with 5% NaOH solution several times, then with the distilled water and dried over freshly fused potassium carbonate. The ether was then removed by distillation and the residual oil was distilled under reduced pressure (Table III).

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STUDIES ON HYDROFLUORENE DERIVATIVES. PART I. SYNTHESIS OF 1:2:3:4:10:11-HEXAHYDROFLUORENE-2-ONE

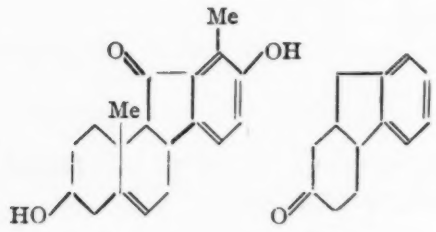
By Beda Prasad Sen, Amareshwar Chatterjee, Santi Kumar Gupta and Bidyut Kamal Bhattacharyya

2-Indanone has been prepared by the Curtius degradation of indene-2-carboxylic acid. The Mannich-Robinson reaction with ethyl hydrind-2-one-1-carboxylate furnishes the desired product (III) in low yield; (III), after cyclisation and decarboxylation, yields 1:2:3:4-tetrahydrofluorene-2-one (IV). (IV) on catalytic reduction affords 1:2:3:4:10:11-hexahydrofluorene-2-one (II). The condensation of methyl 1-keto-2-indanylacetate with methyl succinate yields an acidic material which after esterification furnishes the desired product (V). This, on decarboxylation, followed by esterification and catalytic hydrogenation, furnishes the saturated di-ester (VII) which, on the Dieckmann cyclisation, followed by acid treatment, affords the same hexahydrofluorene-2-one (II).

With a view to synthesising the phenol (I), obtained as a degradation product of jervine (Fried *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 2970; cf. Fried and Klingsberg, *ibid.*, 1953, **75**, 4929), some pilot experiments are described below.

In our previous paper (Chatterjee, Chatterjee and Bhattacharyya, this *Journal*, 1958, **35**, 391) it was noted that the Mannich-Robinson reaction of a mixture of methyl-5-methoxyhydrind-2-one-1- and -5-carboxylates with 1-diethylaminobutanone-3 did not furnish any promising result. But the same reaction with ethyl hydrind-2-one-1-carboxylate afforded the desired product (III) in low yield even when two moles of the β-keto ester were used for one mole of the methoiodide. Cyclisation and decarboxylation of the compound (III) with aqueous alkali resulted in a polymerised product. However, when treated with a mixture of acetic and hydrochloric acids (cf. Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469; Chatterjee and Bhattacharyya, this *Journal*, 1958, **35**, 19), it afforded 1:2:3:4-tetrahydrofluorene-2-one (IV) in poor yield. The ultraviolet absorption spectrum, λ_{max} 257 mμ (log ε 4.07), establishes the location of the double bond at 10:11 positions. The unsaturated compound (IV), which was rather unstable, on hydrogenation over palladium catalyst, furnished the saturated compound (II). The latter compound, on reduction with lithium aluminium hydride, followed by dehydrogenation with selenium, afforded fluorene.

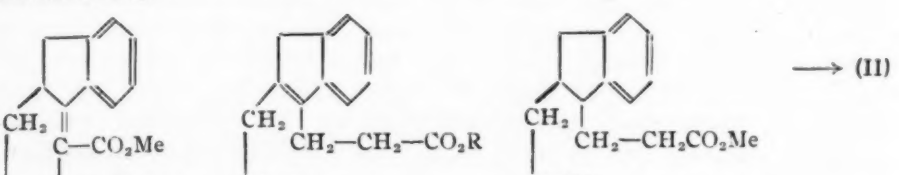
Because of the low yield of this step and our previous experience (Chatterjee, Chatterjee and Bhattacharyya, *loc. cit.*), the Mannich-Robinson reaction with indan-2-one, prepared by the Curtius degradation of indene-2-carboxylic acid, was not attempted.



(I) (II) (III) (IV)

Since the overall yield in the aforementioned preparation of 1:2:3:4:10:11-hexahydrofluorene-2-one is extremely low, another successful synthesis of the compound (II) is reported below.

Although the Stobbe condensations of indan-1-one (Clemo *et al.*, *J. Chem. Soc.*, 1951, 863) and 4-methylindan-1-one (Howell and Taylor, *ibid.*, 1957, 3011) had always yielded the desired products in low yield, the condensation of methyl succinate with methyl 1-keto-2-indanylacetate according to the procedure of Johnson *et al.* (*J. Amer. Chem. Soc.*, 1950, **72**, 2395) afforded an acidic product, which after esterification with diazomethane furnished the desired condensation product (V) in about 40% yield. The ultraviolet absorption spectrum, λ_{max} 272 mμ (log ε 4.1), is indicative of the presence of cinnamic ester system in the compound (V). Treatment of the compound (V) with a mixture of acetic acid, hydrobromic acid and water, following the procedure of Johnson *et al.* (*loc. cit.*), furnished a crystalline acid (VI: R = H). The ultraviolet spectra of this acid, λ_{max} 259 mμ (log ε 4.00), and of its dimethyl ester, λ_{max} 257 mμ (log ε 4.06), indicate that the double bond has shifted from its exocyclic position into the *cyclo*pentane ring. The compound (VI: R = Me) was hydrogenated over palladium charcoal catalyst and the saturated ester (VII), thus obtained, was cyclised with sodium methoxide or by sodium hydride to furnish a β-keto ester, which on hydrolysis and decarboxylation afforded the ketone (II).



(V) (VI) (VII)

Further work along this line is in progress.

* Experimental

2-*Indanone*

For the preparation of indene-2-carboxylic acid, we essentially followed the method of Auwers (*Annalen*, 1918, **415**, 167). But as the yields of the formyl

* All m.p. s are uncorrected. The ultraviolet absorption spectrum was examined in 95% ethanol by the Unicam spectrophotometer SP 500.

compound and indene-2-carboxylic acid have not been reported, the preparation of the formyl compound and the cyclisation of the latter by a modification of the original method are described below.

To sodium dust (2.3 g.) and a drop of methanol in benzene (45 c.c.), cooled to -10°, was added a mixture of ethyl β-phenylpropionate (8.9 g.) and ethyl formate (8 c.c.) in ether (30 c.c.) with shaking under nitrogen atmosphere, and the reaction mixture was allowed to stand for 48 hours. It was worked up and distilled, b.p. 105-10°/2 mm, yield 5.2 g. (reported b.p. 142°/14 mm; V. Auwers, *loc. cit.*).

To a stirred mixture of H_2SO_4 (conc., 200 c.c.) and phosphoric acid (85%, 60 c.c.), cooled to -10°, was added dropwise the above formyl compound (20 g.). After the completion of the addition, the stirring was continued for 2 hours. The dark red reaction product was poured into crushed ice and the product was extracted with ether. The ethereal layer was washed with sodium bicarbonate, dried and distilled to furnish ethyl indene-2-carboxylate (8 g.), b.p. 118°/2 mm; m.p. 50° (reported m.p. 50°). The alkaline aqueous layer was acidified to furnish indene-2-carboxylic acid (3 g.), m.p. 230-34° (reported m.p. 234°). The ester was hydrolysed with 1 : 1 sulphuric acid by refluxing under nitrogen for 2 hours.

The acid (0.5 g.) was treated with thionyl chloride (0.5 c.c.) and a drop of pyridine in ether (15 c.c.). After removal of the ether, the residue (0.5 g.) was dissolved in dry acetone (6 c.c.) and cooled in an ice-bath. To the solution of the acid chloride was added a solution of potassium azide (0.3 g.) in water (0.8 c.c.) with shaking, when a white pasty material separated out. The reaction mixture was allowed to stand for 15 minutes in the cold and then diluted with water (14 c.c.). The precipitated solid was filtered and washed once with water and dried, m.p. 97-100° (decomp.), yield 0.5 g. A mixture of the crude azide (0.5 g.) and ethanol (7 c.c.) was refluxed for 2 hours. After removal of the ethanol, the residue was evaporatively distilled at 150°/4 mm to furnish a crystalline material which on crystallisation from a mixture of acetone and petroleum ether yielded the pure material (0 25 g.), m.p.155°. (Found : N, 6.9. $C_{12}H_{13}O_2N$ requires N, 6.89%).

A mixture of the above urethane (0.2 g.) and 2 *N*-HCl (140 c.c.) was distilled when the solid ketone came out with steam. The ketone was extracted with ether and after evaporation of the ether, the residue was converted into the semicarbazone. The crude semicarbazone (0.14 g.) was crystallised from alcohol to furnish the pure material, m.p. 218° (reported m.p. 218°; Thorpe, *Proc. Chem. Soc.*, 1911, 128). (Found : N, 22.23. (Calc. for $C_{10}H_{11}ON_3$: N, 22.22%.)

3-Carbethoxy-3-butan-3'-onyl indan-2-one (III).—Xylene bromide, prepared by the method of Perkin (*J. Chem. Soc.*, 1888, **53**, 5) was converted into phenylenediacetonitrile according to the method of Moore and Thorpe (*ibid.*, 1908, **93**, 175). Phenylenediacetic acid was prepared from the above dinitrile, following the procedure of Perkin and Titley (*ibid.*, 1922, **121**, 1562). Ethyl 2-hydrindone-1-carboxylate was obtained by the Dieckmann cyclisation of diethylphenylene diacetate according to the method of Carrick and Fry (*J. Amer. Chem. Soc.*, 1955, **77**, 4386).

To the sodio enolate, prepared from the above β-keto ester (10 g.) and sodium dust (0.79 g.) in dry benzene (150 c.c.), was added, under nitrogen atmosphere, the methoiodide of 1-diethylamino-3-butanone (4.3 g. of base), dissolved in absolute alcohol (10 c.c.). The reaction mixture was allowed to stand for 16 hours at room temperature and refluxed for 1 hour. The cooled reaction mixture was poured into ice-water. The benzene layer was washed successively with water, NaOH solution (5 %) and finally with water. The combined aqueous layer and the above washings on acidification with iced HCl furnished the unchanged β-keto ester (3.4 g.). The benzene solution was dried and evaporated. The residue, thus obtained, was evaporatively distilled at 130°/0.1 mm to yield a white crystalline solid (2.8 g.) containing some oily material which was further purified by crystallisation from a mixture of ether and petroleum ether (40-60°) to afford a crystalline material (2.3 g.), m.p. 78-79°. This material even on repeated crystallisation always gave a lower analytical value for carbon and hydrogen. A portion of the above material (750 mg.) was chromatographed on alumina (30 g.) using petroleum ether (60-80°) as the eluting solvent. The liquid fraction (350 mg.), thus obtained, soon solidified. A portion of this solid (200 mg.) was crystallised three times from petroleum ether (40-60°) to furnish a material, m.p. 79-79.5°, which was evaporatively distilled at 125°/0.2 mm for analysis. (Found: C, 70.31; H, 6.30. $C_{16}H_{18}O_4$ requires C, 70.07; H, 6.56%).

1:2:3:4-*Tetrahydrofluorene-2-one* (IV)

(*a*). *Acid cyclisation.*—A mixture of the above crystalline compound (III, 550 mg., m.p. 78-79°), 6*N*-HCl (22 c.c.) and glacial acetic acid (22 c.c.) was heated on a water-bath, under nitrogen, for 4 hours. The reaction mixture was diluted with a large excess of cold water and extracted several times with ether. The solvent was washed successively with water, saturated sodium bicarbonate solution and water. After removal of the dry solvent, the residue obtained was sublimed at 85-90°/0.1 mm to afford a white crystalline material (220 mg.), m.p. 93° with previous shrinking at 75°. This substance was very unstable at room temperature and did not furnish any semicarbazone. The above crystalline material (220 mg.) was chromatographed over alumina (6.6 g.) using petroleum ether as the eluting solvent. The white flaky crystals (140 mg.), thus obtained, was further purified by sublimation at 95-100°/0.4 mm to furnish the pure material, m.p. 95°, λ_{max} 257 mμ (log ε 4.07). (Found: C, 84.89; H, 7.09. $C_{13}H_{12}O$ requires C, 84.72; H, 6.52%).

(*b*). *Alkali cyclisation.*—To the compound (III, 0.4 g.) in boiled water (30 c.c.) was added a solution of KOH (85%, 0.4 g.) in boiled water (10 c.c.). The reaction mixture was refluxed for 2 hours under nitrogen. Then, KOH(1.1 g.), dissolved in boiled water (10 c.c.), was added to make the alkali concentration 2.5%. The resulting mixture was refluxed for 6 hours more. On working up no product could be isolated.

1:2:3:4:10:11-*Hexahydrofluorene-2-one* (II)

The above crude solid compound (IV, 490 mg.), dissolved in ethanol (95%, 30 c.c.), was hydrogenated over palladium charcoal catalyst (10%, 110 mg.). The

theoretical amount of hydrogen was absorbed within one hour. The catalyst was filtered and the oily residue, obtained after evaporation of the solvent, was evaporatively distilled at 85-90°/0.2 mm to furnish a colorless viscous oil (450 mg.), λ_{max} 265 mμ (log ε 3.09).

The *semicarbazone* (100 mg.), m.p. 193° (crude), prepared from the above reduced product (100 mg.), was crystallised three times from methanol to furnish the pure material, m.p. 194-94.5°. (Found: C, 69.04; H, 7.02. $C_{14}H_{17}ON_3$ requires C, 69.13; H, 6.99%).

Dehydrogenation.—The above saturated ketone (300 mg.) was reduced by lithium aluminium hydride (150 mg.) by the usual procedure and the crude alcohol, thus obtained, was dehydrogenated by heating with selenium (500 mg.) at 295-305° for 14 hours. The reaction product was extracted with benzene and ether. The combined solvent was evaporated and the residue was sublimed at 80-95°/0.2 mm to yield a coloured crystalline material (140 mg.), m.p. 114-15°, which was recrystallised two times from methanol to furnish the pure compound, m.p. 116°. Mixed m.p. of this with an authentic sample of fluorene remained undepressed.

Methyl β-Carbomethoxy-β-(2-methylacetate-3-indenylidene)-propionate (V)

2-Bromohydrindone was prepared by following the procedure of Johnson *et al.* (*J. Amer. Chem. Soc.*, 1945, **67**, 1745). This compound was also prepared by Groves and Swan (*J. Chem. Soc.*, 1951, 867). In our case, the temperature of bromination of 1-indanone was maintained at 0-5° throughout the operation. Only the dibromo compound could be isolated as the major product by adding bromine below 10° and then allowing the reaction mixture to stand at the room temperature (30°) for 2 hours. The concentration of the solvent (dry ether) in this reaction (cf. Johnson *et al.*, *loc. cit.*) appeared to be an important factor to avoid the formation of the dibromo compound.

Ethyl 1-keto-2-indanylmalonate was prepared from the above bromo compound according to the method of Groves and Swan (*loc. cit.*). The decarboxylation of the malonic ester system in the present case (cf. Groves and Swan, *loc. cit.*) was performed by refluxing the compound (18.1 g.) with a mixture of HCl (conc., 180 c.c.) and water (180 c.c.) for 24 hours. The mixture, on cooling in ice-bath, deposited 1-keto-2-indanylacetic acid (10 g.), m.p. 147°, which on crystallisation from hot water furnished the pure acid, m.p. 150-51° (reported m.p. 147-40°; Groves and Swan, *loc. cit.*).

The above crude acid (13 g.), on esterification with absolute methanol (100 c.c.) and H_2SO_4 (conc., 6 c.c.) by refluxing for 10 hours, afforded methyl 1-keto-2-indanylacetate (11.88 g.), b.p. 164-65°/1.5 mm.

Dimethyl succinate (11.63 g.) was added to a solution of potassium (2.2 g.) in dry *tert.*-butyl alcohol (42 c.c.) at room temperature (nitrogen atmosphere) and the mixture was stirred till homogeneous. To this solution was added the above keto-ester (7.88 g.) with *tert.*-butyl alcohol (8 c.c.) and the mixture was stirred

for 2 hours. As the yellow solution stood for 24 hours at room temperature (nitrogen atmosphere), it gradually turned to a deep red colour. The reaction mixture was then acidified with HCl (dil.) and most of the alcohol was distilled off at a reduced pressure. The pale yellow oily residue was taken up in ether and extracted with saturated sodium bicarbonate solution. The combined extract was acidified and the precipitated oil was taken up in ether. The ethereal layer was dried over anhydrous sodium sulphate. The yellow oily product, obtained on evaporation of the ether and removal of traces of the solvent, was esterified by refluxing with dry methanol (100 c.c.) and H_2SO_4 (conc., 6 c.c.) for 12 hours. After usual working up, the residue, obtained after evaporation of the solvent, was distilled giving the desired unsaturated trimethyl ester as a straw-coloured oil (4.45 g.), b.p. 200-205°/0.4 mm, λ_{max} 272 mμ (log ε 4.14) and 300 mμ (log ε 4.00), leaving a higher boiling residue (3 g.). (Found: C, 65.17; H, 6 33 $C_{18}H_{20}O_6$ requires C, 65.06; H, 6.02%). It may be mentioned that the esterification of the Stobbe product with diazomethane did not improve the yield of the compound (V).

The neutral ether extract from the above condensation was washed with water, dried, the ether removed, and the residue distilled, furnishing the unchanged keto-ester (0.65 g.), b.p. 150-55°/0.8 mm.

β-(2-*Carboxymethyl*-3-*indenyl*)-*propionic Acid* (VI: R=H).—The above unsaturated ester (4 g.) was refluxed for 3-4 hours with a mixture of glacial acetic acid (60 c.c.), HBr (48%, 40 c.c.) and water (20 c.c.). The acids were removed under reduced pressure and the residue, on cooling and diluting with cold water, deposited a coloured solid material which was filtered and dried to give the desired unsaturated acid (3.30 g.), m.p. 173-74°. A part of this material was crystallised two times from a mixture of ether-petroleum ether (60-80°) to furnish a fairly pure acid, m.p. 178-79°, which was recrystallised from dilute methanol (33%) to yield the pure acid, m.p. 179-80°, λ_{max} 259 mμ (log ε 4.00). (Found: C, 68.27; H, 5.80. $C_{14}H_{14}O_4$ requires C, 68.29; H, 5.69%).

Methyl β-(2-*Methylacetate*-3-*indenyl*)-*propionate* (VI: R = Me).—The above unsaturated acid (1.65 g.), on esterification by an ethereal solution of diazomethane, prepared from nitrosomethylurea (4 g.), furnished the desired unsaturated ester (1.4 g.), evaporatively distilling at 120-25°/0.2 mm, λ_{max} 257 mμ (log ε 4.06). (Found: C, 70.45; H, 6.70. $C_{16}H_{18}O_4$ requires C, 70.07; H, 6.56%).

Methyl β-(2-*Methylacetate*-3-*indanyl*)-*propionate* (VII).—The above unsaturated ester (1.1 g.) was catalytically reduced by 10% palladium on charcoal catalyst (200 mg.), as described before. The absorption of hydrogen, which was very fast at the start, was completed within one hour. The residue, obtained after removal of the catalyst and the solvent, was evaporatively distilled at 125-30°/0.4 mm to yield an oil (1.07 g.), λ_{max} 264 mμ (log ε 3.04). A portion was again evaporatively distilled for analysis. (Found: C, 69.32; H, 7.43. $C_{16}H_{20}O_4$ requires C, 69.56; H, 7.24 %).

1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorene-2-one* (II)

(*a*). The above saturated ester (1.07 g.) was cyclised by refluxing for 6 hours with sodium hydride (0.17 g.) under dry benzene (25 c.c.) containing two drops of methanol. The reaction mixture was cooled, acidified with HCl (dil.) and extracted three times with ether. The combined extract was washed with cold water, dried and evaporated to give an oily residue which produced a deep violet coloration with alcoholic ferric chloride solution. The residue was then hydrolysed by refluxing for 16 hours with 6*N*-HCl (50 c.c.). The cooled reaction mixture was worked up by the usual procedure and the neutral ketone, thus obtained, was evaporatively distilled at 85-95°/0.2 mm to afford an oil (0.27 g.). The *semicarbazone* (100 mg.), m.p. 193°, obtained from the above ketone (100 mg.), was crystallised from methanol to furnish the pure material, m.p. 194°. The mixed m.p. of this semicarbazone with that obtained before, remained undepressed.

(*b*). The saturated ester (1.4 g.) was cyclised by refluxing for 6 hours with sodium methoxide, prepared from sodium dust (0.23 g.) and methanol (0.4 c.c.) in dry benzene (25 c.c.). After usual working up, the crude β-keto ester was hydrolysed by refluxing for 8 hours under nitrogen with a mixture of HCl (conc., 8 c.c.), glacial acetic acid (10 c.c.) and water (4 c.c.). The reaction mixture was cooled, diluted with water and extracted two times with ether. The aqueous layer was neutralised by sodium bicarbonate and extracted three times with ether. The combined extract was washed with cold alkali solution (2%) and finally with water. After removal of the dry solvent, the neutral residue was evaporatively distilled at 90-100°/0.4 mm to furnish the desired ketone (0.46 g.). A pure sample, λ_{max} 256 mμ ($\log \epsilon$ 3.09), was prepared for analysis by repeated evaporative distillation. (Found : C, 83.67; H, 7.58. $C_{13}H_{14}O$ requires C, 83.87 ; H, 7.52%).

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*iso*QUINOLINE DERIVATIVES. PART IV

By T. N. Ghosh, Bhabatosh Bhattacharya and Saktipada Dutta

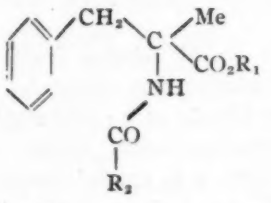
Treatment of α-methyl-α-acetamido-β-phenylpropionic acid with a mixture of polyphosphoric acid and phosphorus oxychloride leads to the formation of 1 : 3-dimethyl*iso*quinoline, the process involving cyclodehydration, probably followed by decarboxylation and then dehydrogenation.

Snyder and Werber (*J. Amer. Chem. Soc.*, 1950, **72**, 2962) made an interesting observation that when *N*-acetylphenylalanine was subjected to the Bischler-Napieralski reaction with a mixture of polyphosphoric acid and phosphorus oxychloride, 1-methyl*iso*quinoline was formed, the process involving cyclodehydration, decarboxylation and dehydrogenation. The exact sequence of the three processes involved has not been established. An observation of a similar nature has also been made from this laboratory (Ghosh and Dutta, this *Journal*, 1955, **32**, 17, 755) in that, when (α-acetamido-β-phenyl)-ethylmethyl ketone or β-phenyl-substituted analogues are treated with either phosphorus oxychloride or concentrated sulphuric acid, 1-methyl*iso*quinoline derivatives are formed, the process involving cyclodehydration, deacetylation and dehydrogenation.

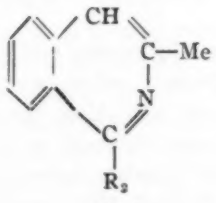
It has been considered desirable at this stage to investigate the mechanism of the above reaction. That cyclodehydration may be the first step is suggested by the observation of Brodrick and Short (*J. Chem. Soc.*, 1949, 2587) who have found that certain 3 : 4-dihydro*iso*quinolines lose hydrgen atoms when distilled at atmospheric pressure to furnish fully aromatised compounds. Clemo and Hoggarth (*ibid.*, 1954, 95) have observed that 1 : 2 : 3 : 4-tetrahydro*iso*quinoline-3-carboxylic acid on boiling in ethanol containing sulphuric acid, dehydrogenates to give rise to 3 : 4-dihydro*iso*quinoline 3-carboxylic ester. Reference is also made to the observation of Harwood and Johnson (*J. Amer. Chem. Soc.*, 1934, **56**, 468) that 6 : 7-dimethoxy-1-phenyl-3 : 4-dihydro*iso*quinoline-3-carboxylic acid, when treated with thionyl chloride, is transformed into the corresponding fully aromatised acid chloride with the loss of two hydrogen atoms. However, some experiments, which have been designed to investigate the sequence of the three processes involved during the Bischler-Napieralski reaction of substituted *N*-acetyl- or *N*-benzoylphenylalanine, are now described in this paper.

It has now been found that when α-methyl-α-acetamido-β-phenylpropionic acid (I : R_1 = H ; R_2 = Me) or its ester (Ghosh, Bhattacharya and Datta, this *Journal*, 1957, **34**, 417) is treated with a mixture of polyphosphoric acid and phosphorus oxychloride, a base is obtained as a picrate which has been identified as the picrate of of 1 : 3-dimethyl*iso*quinoline (II : R_2 = Me) (Witkop, *J. Amer. Chem. Soc.*, 1948, **70**, 1424). Similarly, the α-benzamido analogue, under identical condition, has been found to yield a base, identified as 1-phenyl-3-methyl*iso*quinoline (II : R_2 = Ph) (Whaley and Hartung, *J. Org. Chem.*, 1949, **14**, 650). These observations obviously show that in

the above reactions decarboxylation has taken place prior to dehydrogenation, as otherwise there is no hydrogen atom at the α-position to the carboxy group in (I) which could be removed. The next point which remains to be settled is whether cyclodehydration has taken place prior to decarboxylation and dehydrogenation or not. With this object in view, 1 : 3-dimethyl-3-carbethoxy-3 : 4-dihydro*iso*quinoline (III : R_1 = Et ; R_2 = Me) and also the corresponding 3-carboxy compound have been treated with a mixture of polyphosphoric acid and phosphorus oxychloride under conditions as employed in the case of (I : R_1 = H ; R_2 = Me), and in each case 1 : 3-dimethyl*iso*quinoline (II : R_2 = Me) has been obtained and identified as picrate. This conversion has also been effected by heating (III : R_1 = Et; R_2 = Me) with concentrated alkali (25%) for a prolonged period. All the above observations, when considered, tend to show that in the Bischler-Napieralski reaction of α-methyl-α-acetamido-β-phenylpropionic acid or its ester to furnish 1 : 3-dimethyl*iso*quinoline, cyclodehydration is probably the first step that is involved, followed by decarboxylation and then dehydrogenation.



(I)



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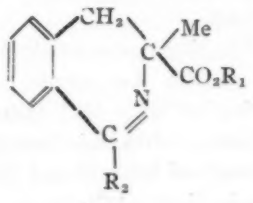

(III)

EXPERIMENTAL

Cyclisation of α-Methyl-α-acetamido-β-phenylpropionic Acid (I : R_1 = H ; R_2 = Me) : *Formation of* 1 : 3-*Dimethyliso*quinoline.—In a flask, protected from moisture, P_2O_5 (150 g.) was treated with orthophosphoric acid (85%, 98 c.c.) and the mixture heated on a steam-bath for 2 hours with occasional shaking. To the cooled syrupy mass the compound (I : R_1 = H ; R_2 = Me ; 18.8 g.) and $POCl_3$ (30.4 c.c.) were added and the mixture, after thorough shaking, was heated at 125° for 8 hours. After cooling, the mixture was treated with ice-water (charcoal) and filtered. The filtrate was basified with NaOH solution under cooling and the liberated red oil was extracted with ether. After removal of the ether, the oil (3 g.) was purified by HCl-NaOH treatment and it furnished in benzene solution a picrate which crystallised from ethanol in yellow needles, m.p. 181-82°, undepressed on admixture with an authentic sample of the picrate of 1 : 3-dimethyl*iso*quinoline (Witkop, *loc. cit.*). (Found : C, 52.64 ; H, 3.92 ; N, 14.59. Calc. for $C_{11}H_{11}N.C_6H_3O_7N_3$: C, 52.85 ; H, 3.62 ; N, 14.51%).

The same base, characterised as picrate, was obtained when the ester (I : R_1 = Et ; R = Me) was similarly treated with a mixture of polyphosphoric acid and $POCl_3$.

Cyclisation of α-Methyl-α-benzamido-β-phenylpropionic Acid (I : R_1 = H ; R_2 = Ph) : *Formation of* 1-*Phenyl-3-methyliso*quinoline.—The benzamido compound was prepared according to the method of Ghosh, Bhattacharya and Datta (*loc. cit.*) and the method of procedure for cyclisation was the same as described above. The isolated base was a

heavy oil which gradually solidified. It was triturated with ligroin (b.p. 60-80°) and crystallised from EtOH in colorless, shining plates, m.p. 90-91°. (Found: C, 87.28; H, 5.92; N, 6.54. $C_{16}H_{13}N$ requires C, 87.67; H, 5.93; N, 6.39%). Whaley and Hartung (*loc. cit.*), who did not describe the method of crystallisation of the above base, recorded m.p. 123-25°.

1:3-*Dimethyl*-3-*carbethoxy*-3:4-*dihydroisoquinoline* (III: R_1 = Et; R_2 = Me) was prepared in an analogous manner as the corresponding 3-carbomethoxy compound, described previously (Ghosh, Bhattacharya and Datta, *loc. cit.*), but the yield was improved by the following modification: A mixture of ethyl α-acetamido-α-methyl-β-phenylpropionate (34.2 g.), benzene (342 c.c.) and $POCl_3$ (34.2 c.c.) was heated under reflux on a steam-bath for 4 hours. After distilling off benzene and excess of $POCl_3$, the residue was treated with a cold aqueous NaOH solution (5%), and extracted with ether. The ether extract was shaken with HCl (dilute) and the acid extract, on basification with cold dilute NaOH solution, furnished a dark, heavy oil, distilling at 132-34°/2-3 mm to a colorless oil (14.4 g). (Found: N, 6.08. $C_{14}H_{17}O_2N$ requires N, 6.06%).

The above ester was hydrolysed by heating with a dilute NaOH solution (10%) on a steam-bath for about 30 minutes, when a clear solution was obtained. On acidification with HCl (dilute) and scratching, the *hydrochloride* of 1:3-dimethyl-3-carboxy-3:4-dihydro*iso*quinoline was obtained as a crystalline solid, which was recrystallised from ethanol (95%) in colorless, rectangular plates, m p. 179-80°(decomp.). (Found: N, 5.92; Cl, 14.34. $C_{12}H_{13}O_2N$. HCl requires N, 5.84; Cl, 14.82%). The characteristics of this acid have been erroneously recorded in Part III (Ghosh, Bhattacharya and Datta, *loc. cit.*).

Action of a Mixture of Polyphosphoric Acid and $POCl_3$ *on* (III: R_1 = Et; R_2 = Me): *Formation of* 1:3-*Dimethylisoquinoline*.—The method of procedure was the same as described previously. The reaction mixture was cooled, treated with ice-water and filtered from slight impurity. The filtrate was basified with NaOH and the liberated base (a red oil) was extracted with ether and purified by acid-alkali treatment. The picrate, obtained in benzene solution, was crystallised from ethanol in yellow needles, m.p. 181-82°, undepressed on admixture with an authentic sample of the picrate of 1:3-dimethyl*iso*quinoline (Witkop, *loc. cit.*). (Found: N, 14.48. Calc. for $C_{11}H_{11}N.C_6H_3O_7N_3$: N, 14.51%). 1:3-Dimethyl*iso*quinoline was also isolated on subjecting 1:3-dimethyl-3-carboxy-3:4-dihydro*iso*quinoline hydrochloride to the reaction of a mixture of polyphosphoric acid and $POCl_3$ under identical conditions.

When a mixture of (III: R_1 = Et; R_2 = Me) and an aqueous NaOH solution (25%) was heated under reflux on the steam-bath for 16 hours and the mixture cooled and extracted with ether, the ethereal extract yielded a base, the picrate of which was identified to be the picrate of 1:3-dimethyl*iso*quinoline.

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SHORT NOTES

DOUBLE SALTS OF OXYFLUOBORATES WITH SULPHATES AND FLUOBERYLLATES

By Asim Bikash Ray

Double salts are generally formed between alkali metals and those of bivalent or trivalent metals. The important double salts formed by the sulphates are the schonites and alums.

The pure alkali metal or ammonium oxyfluoborates have not yet been isolated. The addition of calculated amounts of alkali fluoride or ammonium fluoride and hydrofluoric acid to boric acid results in the formation of fluoborates and hydroxyfluoborates. The double salts of ammonium sulphate or fluoberyllate with the oxyfluoborates of the bivalent metals have been prepared.

As these anions, e.g., SO_4^{2-}, BeF_4^{2-} and BF_3O^{2-}, are isomorphous, it is very difficult to obtain the double salts with 1 : 1 proportion. Isomorphous replacement invariably takes place and the ratios of SO_4^{2-} or BeF_4^{2-} to BF_3O^{2-} in the final compounds depend upon their respective solubilities. In this paper the analysis of only those crops are given where the ratios of the anions are approximately 1 : 1.

Procedure.—Concentrated solutions of equimolecular proportions of ammonium sulphate or fluoberyllate and oxyfluoborates were mixed and allowed to evaporate at room temperature in a vacuum desiccator over H_2SO_4 (conc.). The first crop which appeared after one or two days was rejected as it was liable to contain a greater proportion of sulphates or fluoberyllates, as the case might be. The next crop was isolated. It was filtered under suction, washed once with water and then with 60% alcohol and dried in air. In subsequent crops, the proportions of the sulphate or fluoberyllate to the oxyfluoborate remained almost constant. In all these compounds the percentages of SO_4^{2-} were higher than those required for 1 : 1 replacement. This is obviously due to the lower solubilities of the pure sulphate double salts. But in the case of fluoberyllate, almost theoretical percentages were obtained due to the higher solubility of these double salts than those containing sulphate.

Ammonium sulphate - copper oxyfluoborate hexahydrate was obtained from ammonium sulphate and copper oxyfluoborate pentahydrate. It is a pale blue crystalline substance, indistinguishable from the double sulphate. [Found : SO_4, 25.85 ; B, 2.68. $(NH_4)_2SO_4.CuBOF_3.6H_2O$ requires SO_4, 24.77 ; B, 2.79%].

Ammonium sulphate - nickel oxyfluoborate hexahydrate is a pale green crystalline substance, obtained from ammonium sulphate and nickel oxyfluoborate hexahydrate. [Found : SO_4, 26.00 ; B, 2.70. $(NH_4)_2SO_4.NiBOF_3.6H_2O$ requires SO_4, 25.10 ; B, 2.83%].

Ammonium sulphate - cobalt oxyfluoborate hexahydrate was obtained from ammonium sulphate and cobalt oxyfluoborate heptahydrate. It is a soluble and pink-coloured substance. [Found : SO_4, 25.77 ; B, 2.69. $(NH_4)_2SO_4.CoBOF_3.6H_2O$ requires SO_4, 25.09 ; B, 2.82%].

Ammonium sulphate - zinc oxyfluoborate hexahydrate. [Found : SO_4, 25.21 ; B, 2.60. $(NH_4)_2 SO_4.ZnBOF_3.6H_2O$ requires SO_4, 24.68 ; B, 2.78%].

Ammonium sulphate - cadmium oxyfluoborate hexahydrate was obtained as a white crystalline substance by mixing concentrated solutions of the constituents. It was washed with 60% alcohol in which $CdBOF_3$, $8/3\ H_2O$ was soluble but not the double salt. [Found : SO_4, 22.48 ; B, 2.40. $(NH_4)_2 SO_4.CdBOF_3.6H_2O$ requires SO_4, 22.02 ; B, 2.48%].

Ammonium fluoberyllate - copper oxyfluoborate hexahydrate was obtained, as described above, as a pale blue crystalline substance. [Found : F, 34.80 ; Be, 2.44. $(NH_4)_2\ BeF_4.CuBOF_3.6H_2O$ requires F, 35.34 ; Be, 2.39%].

Ammonium fluoberyllate - cadmium oxyfluoborate hexahydrate was obtained in the same way as described above. It is a colorless, crystalline, non-hygroscopic substance. [Found : Be, 2.20 ; B, 2.34. $(NH_4)_2\ BeF_4.CdBOF_3.6H_2O$ requires Be, 2.11 ; B, 2.54%].

Ammonium fluoberyllate - zinc oxyfluoborate hexahydrate. [Found : F, 34.73 ; Be, 2.34. $(NH_4)_2\ BeF_4.ZnBOF_3.6H_2O$ requires F, 35.18 ; Be, 2.38%].

Ammonium fluoberyllate - nickel oxyfluoborate hexahydrate was obtained in the same way as the copper compound, as a pale green crystalline substance. [Found : F, 38.0 ; Be, 2.40. $(NH_4)_2\ BeF_4.NiBOF_3.6H_2O$ requires F, 38.49 ; Be, 2.42%].

Ammonium fluoberyllate - cobalt oxyfluoborate hexahydrate is a pink-coloured crystalline substance, fairly soluble in water. [Found : Be, 2.54 ; B, 2.76. $(NH_4)_2$-$BeF_4.CoBOF_3.6H_2O$ requires Be, 2.42 ; B, 2.90%].

The author takes this opportunity to express his gratitude to Prof. N. N. Ray, D. Sc., of Presidency College, Calcutta and to Prof. G. P. Mitra, D. Sc., of City College, Calcutta for their kind interest during the progress of the work and offering all the laboratory facilities.

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STUDIES ON MAHUA STEROL FROM *BASSIA LATIFOLIA*

By P. N. Bhargava and R. P. Singh

Bassia latifolia or *Madhuka indica*, known in Hindi as 'Mahua' and in Sanskrit as 'Atavimadhuka' is one of the abundantly growing plants in India. The fruit of the plant is highly medicinal and the oil therefrom is much used by the hill tribes in the treatment of scurvy.

The fat obtained from the kernels of the plant is known as 'Mahua butter' in Hindusthani and 'Illipe butter' in English. From a survey of literature, it is concluded that the earlier workers could throw no light on the chemical constitution of the unsaponifiable matter of Mahua oil. This led the authors to investigate the nature of the unsaponifiables.

The present investigation reveals that Mahua oil contains 2.53% of unsaponifiable matter and a gummy semisolid mass, which makes up the rest. From this unsaponifiable matter, two sterols, m.p. 117° and 122° respectively, have been isolated by chromatographic method. The higher melting sterol on fractional crystallisation, according to the technique adopted by Anderson (*J. Amer. Chem. Soc.*, 1926, **48**, 2976, 2987), showed no further alteration in specific rotation. Its molecular formula is found to be $C_{29}H_{50}O$. It appears to be isomeric with β- and γ- sitosterols (Windaus, *Ber.*, 1933, **66**, 1254, 1689; Dirscel, *Z. physiol. Chem.*, 1939, **257**, 239) but possesses a higher specific rotation $[\alpha]_D^{30} - 57°.9$ (chloroform) and lower m.p. 122° than any of the isomeric sterols. It has been found to contain one double bond, and one hydroxyl group. The characteristics of the sterol have further been confirmed by the formation of a digitonide, m.p. 220° (decomp.) and liberation of the original sterol, showing the presence of a 3-β-hydroxyl group in the molecule.

Isolation of Sterol.—The oil (2 kg.) (obtained from the seeds in 41% yield) was saponified with 20% NaOH solution and extracted with petroleum ether. The extract after washing with water and drying over calcium chloride was distilled, when 43.8 g. of the unsaponifiable matter was obtained. This product was dissolved in methyl alcohol and kept in a frigidaire overnight, when the precipitate of the sterol (20.3%) and a large amount of a brown gummy residue (79.7%) were obtained. The precipitate after dissolution in petroleum ether and keeping in a frigidiare, melted at 112-18°. This crude product was separated into two sterols: (1) m.p. 117°, $[\alpha]_D^{30} - 43°.5$ ($CHCl_3$) and (2) m.p. 120-22°, $[\alpha]_D^{30} - 57°.5$ ($CHCl_3$).

Fractionation of Mahua Sterol.—The product (7.15 g.), obtained above, was fractionated by repeated crystallisations from ether-alcohol mixture and finally crystallised from absolute alcohol, when colorless plates, m.p. 117°, $[\alpha]_D^{30} - 43°.7$, were obtained. This product being in a minute quantity and impure, could not be used for further investigation.

Mahua sterol crystallises in flakes, m.p. 122°. It is soluble in benzene, chloroform and petroleum ether but sparingly soluble in cold methyl or ethyl alcohol. It gives positive Salkowski's reaction and in the Liebermann-Burchard reaction it assumes a pink colour, which quickly changes to green. In the Steinle-Khlenberg reaction, a purple coloration is observed, which on exposure to light turns cobalt blue. (Found: C, 84.23 ; H, 11.98. M. W., 430. $C_{29}H_{50}O$ requires C, 84.05 ; H, 12.08%).

Monoacetyl derivative of the Mahua sterol was prepared as usual and crystallised from absolute alcohol in needles, m.p. 113-14°, $[\alpha]_D^{30} - 52.9°$, yield 80 3%. (Found: C, 81.46 ; H, 11.38. $C_{31}H_{52}O_2$ requires C, 81.58 ; H, 11.4%).

Monobenzoyl derivative of the product was obtained as usual and was crystallised from ethyl acetate in clusters, m.p. 130°, $[\alpha]_D^{30} - 26°.5$ ($CHCl_3$). (Found: C, 83.52 ; H, 10.38. $C_{36}H_{54}O_2$ requires C, 83.4 ; H, 10.42%).

Digitonide derivative was prepared by heating under reflux a mixture of sterol (0.5 g.) and digitonin (0.5 g.), dissolved in alcohol for 2 hours and keeping the contents in a frigidaire overnight. The fluocculent precipitate was washed with alcohol and ether and dried. The compound melted at 220°. (Found: C, 61.86 ; H, 8.58. $C_{29}H_{50}O.C_{55}H_{90}O_{29}$ requires C, 61.91 ; H, 8.6%).

Mahua sterol acetate dibromide.—The sterol acetate was brominated by the method of Windaus and Hauth (*Ber.*, 1906, **39**, 4378). The sterol acetate dibromide formed a slightly yellowish amorphous powder, m.p. 108°. (Found: Br, 25.88. $C_{31}H_{52}O_2Br_2$ requires Br, 25.97%).

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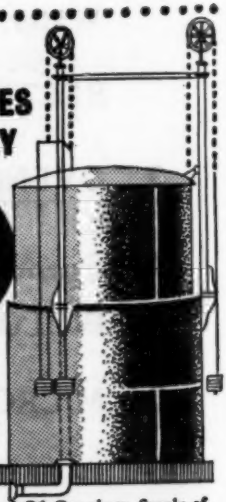

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